

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Recovery and reuse of  $\text{TiO}_2$  and other  
pigments from paint waste

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Department of Chemical and Biological Engineering

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Gothenburg, Sweden 2014

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# Recovery and reuse of $\text{TiO}_2$ and other pigments from paint waste

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## Abstract

Titanium dioxide ( $\text{TiO}_2$ ) has numerous applications in our society, most notably as a white pigment in products such as paint, paper and plastic. Since 2010 there has been a sharp increase in the demand for and price of  $\text{TiO}_2$ . As a result new and innovative ways of  $\text{TiO}_2$  production are needed. One potential source for recovering of  $\text{TiO}_2$  could be from waste paint. Not only could a recycling or recovery process for paint residues give paint manufacturers a new source of pigment, it would also give the industry a way of handling production waste and leftover paint products.

In this work the possibility of replacing virgin pigments with inorganic residues from a waste paint pyrolysis process has been investigated.  $\text{TiO}_2$  and commonly used extender pigments were characterised using thermogravimetric analysis (TGA), X-ray diffraction (XRD) and specific surface area measurements (BET- $\text{N}_2$ ) before and after the pyrolysis process. The inorganic residues from the pyrolysis were used in two different types of paint formulations as pigment replacement. The properties of the paints based on the pyrolysis residues were compared to the properties of paints based on virgin material.

Results showed the crystal structures of the major pigments were left intact following the pyrolysis recovery process. Additionally, the recovery process had a negligible effect on the surface areas of all pigments except  $\text{TiO}_2$ . The paints made from recycled material had acceptable opacity and gloss, but also showed surface defects due to poorly dispersed pigments and a decrease in whiteness.

**Keywords:** Titanium dioxide, Recovery, Paint Waste, Pyrolysis

## List of Publications

This work is based on the work presented in:

### Paper I

Mikael Carl Fredrik Karlsson, Daniel Corr, Christer Forsgren, Britt-Marie Steenari, *Recovery of titanium dioxide and other pigments from waste paint by pyrolysis*, Manuscript

**Contribution:** Main author, all experimental work and evaluation of data except paint formulation and evaluation

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## Introduction

The U.S. Geological Survey has estimated that in 2011 the total world mining production of rutile and ilmenite ore, the two major titanium minerals, was 6.7 million metric tonnes [1]. Only about 5% of the mined titanium minerals are used to produce metallic titanium, the rest are used for the production of titanium dioxide [2]. Rutile ore normally has a titanium dioxide content of 94-96%, which makes it the preferred feedstock. Ilmenite, with a titanium content corresponding to 50-60% of  $\text{TiO}_2$  occurs in larger amounts as ore but it needs to be upgraded to “titanium slag” (which contains about 80%  $\text{TiO}_2$ ) or “synthetic rutile” (with 94%  $\text{TiO}_2$ ) [3]. Despite having a lower  $\text{TiO}_2$  content than rutile, in 2009 ilmenite supplied 90% of the world’s demand for titanium minerals and ilmenite will continue to be a major source of titanium in the future. [4]. The main titanium dioxide producing regions are Australia and Africa, but production can be found all across the globe, see Figure 1. About 90% of the  $\text{TiO}_2$  is used as a pigment and the majority of this is in paint and coatings. The consumption is tightly correlated to the amount of disposable income. As the income increases so does the demand for titanium dioxide. Due to the heavy use of titanium dioxide in architectural coatings the activity in the construction industry has an especially strong effect on the titanium dioxide demand. The rapid economic growth in China over recent years has led to increased demand of  $\text{TiO}_2$  and a steep price increase. The price of high grade natural rutile was 500 USD per ton in 2010 and about 2500 USD per ton in early 2012. In the same period the pigment price increased by roughly 35%. [3, 5].

The production of  $\text{TiO}_2$  is the source of large quantities of waste. The European Union has recognized the environmental impact of titanium dioxide production and has thus placed restrictions on the amount of titanium dioxide that is allowed to be used in paint formulations in order to qualify for the voluntary EU Ecolabel [6]. This, together with economic reasons, has made the coatings industry take action to reduce their use of titanium dioxide and to use lower grade material for applications where this is possible.



Figure 1 Titanium feedstock producers worldwide (marked in black) [5].

Due to the high demand for titanium dioxide, the increased price level and the high environmental impact of producing virgin titanium dioxide, new innovative ways of titanium dioxide production are needed. A possible new source of titanium dioxide can be recovery, either in the form of metal or oxide, from different waste materials. Today a recycling process for titanium metal is operational, but processes for recovery of titanium dioxide are non-existent. Titanium dioxide is used in various kinds of products but paint waste is a good starting point from a recovery perspective as the titanium dioxide content is relatively high and paint waste is both plentiful and reasonably homogeneous compared to other waste streams. Not only could a recycling or recovery process give paint manufacturers a new source of pigment, it would also give the industry a way of handling production waste and leftover paint products.

The reuse of old paint, either directly or as a component in new batches of paint, is probably the soundest approach. Initiatives in this direction have been made. Leftover paint is collected and processed and products based on recycled paint are today sold to individuals [7]. Another initiative is the Community Repaint organisation in United Kingdom that is collecting and distributing usable waste paint to people and organisations needing paint. In 2013 this organisation transferred over 245,000 litres of paint to community groups, charities, voluntary organisations and people in social need [8]. However, this option is not always applicable due to dry non-dispersible paint lumps, incompatible paint components, microbiological contamination and the changing chemical and biocide regulations that would make the new paint batch unusable from a legal perspective. Instead the main existing waste management processes for paint described in literature have been designed with the aim to reduce the volumes of waste paint and the residues from various waste treatments. In Sweden paint cans and paint waste together are a major part of the hazardous waste streams from households and industry, respectively. The packaging is normally sorted separately and put into a recycling stream while the paint residues are incinerated and the resulting ashes are landfilled [9].

Gasification or pyrolysis of paint waste or used plastic paint containers as a method for recycling of paint components, or at least the value of these components, have been described in several papers in the literature. Only the organic components in the paint have been viewed as the valuable part that could be used for energy production, while the waste treatment has only been seen as way to reduce the amount of waste [10-14]. No work on the recovery of the inorganic parts (pigments) has been found in the literature so far. In this work the inorganic pigments are considered to be the most valuable and interesting part of the waste paint. This is based on the fact that the price of titanium dioxide pigments and high grade titanium containing feedstock (rutile) for titanium dioxide production has increased considerably during recent years. This has made the paint industry interested in the development of methods to recycle the titanium pigment.

The objective of the work presented in this thesis was to investigate if the inorganic residues from a waste paint pyrolysis process could be used to replace virgin pigments and fillers in paint formulations. A pyrolysis process based on microwave heating was used to separate the inorganic waste fraction from the organic fraction and the water. Waste paint was modelled using a white paint formulation based on rutile and several different inorganic extender



pigments. To simplify the system coloured inorganic pigments were not included in the study. Gas and oil produced from the pyrolysis fraction could potentially be used as an energy source or a raw material for synthesis of chemicals, but this was beyond the scope of this work. A pre-study for a hydrometallurgical recovery of titanium was also included where rutile was leached with strong acids. The purpose of acid leaching was to determine if a hydrometallurgical recovery route could be used as an alternative to pyroprocessing.

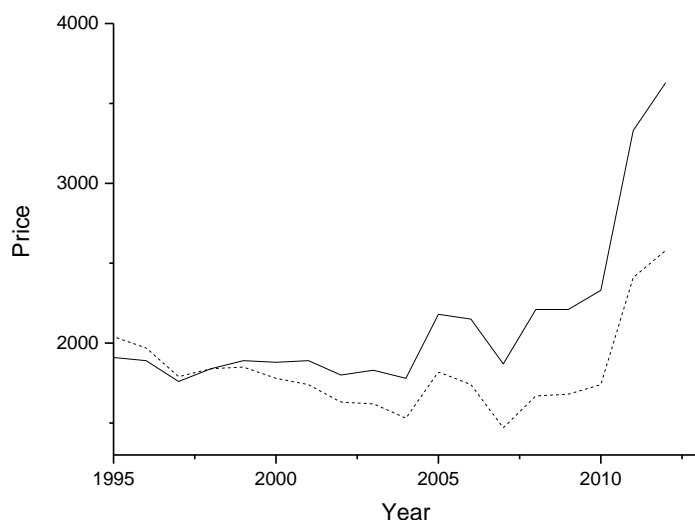


Figure 2 History of the price of titanium pigment from 1995 to 2012. Solid line is price in USD per metric tonne while the dashed line is the price per metric tonne converted to the USD value of 1998 [15].

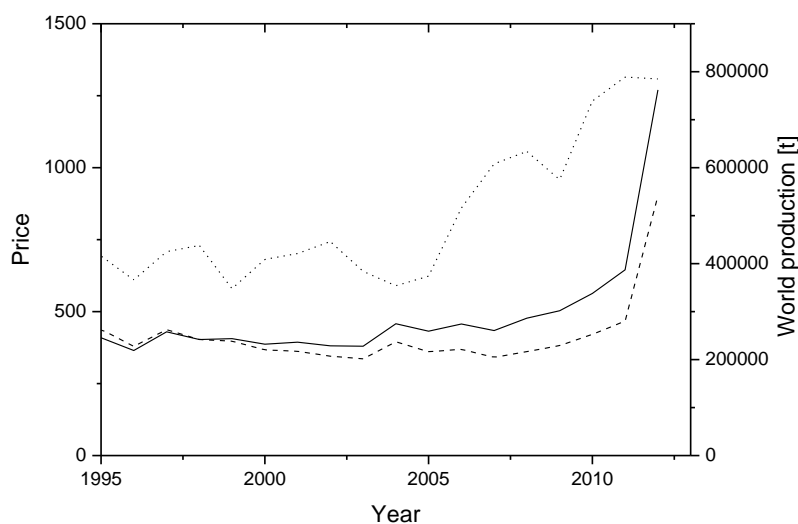


Figure 3 History of the price of natural and synthetic rutile from 1995 to 2012. Solid line is price in USD per metric tonne while the dashed line is the price per metric tonne converted to the USD value of 1998. Dotted line is the estimated world production of natural and synthetic rutile in metric tonnes [15].

## Background

### Titanium dioxide

The titanium concentration in the earth's crust is roughly 0.6 weight per cent and there are several different minerals containing titanium, see Table 1 for an overview. This makes titanium the ninth most common element in the crust. Titanium dioxide is, from a technological perspective, by far the most important of the titanium compounds. Approximately 90% of all titanium dioxide is used as a white pigment [16].

Pure titanium dioxide is a colourless crystalline solid and it occurs in nature in three different crystal forms: Tetragonal rutile, tetragonal prisms of anatase and orthorhombic brookite. Some general properties of these compounds can be found in Table 2.

Table 1 Minerals containing titanium [4].

Mineral	Composition	TiO <sub>2</sub> content in per cent
<b>Rutile</b>	TiO <sub>2</sub> (tetragonal, twinned)	~95
<b>Anatase</b>	TiO <sub>2</sub> (tetragonal, near octahedral)	~95
<b>Brookite</b>	TiO <sub>2</sub> (orthorhombic)	~95
<b>Ilmenite</b>	FeO·TiO <sub>2</sub>	40-65
<b>Leucoxene</b>	Fe <sub>2</sub> O <sub>3</sub> ·nTiO <sub>2</sub>	>65
<b>Arizonite</b>	Fe <sub>2</sub> O <sub>3</sub> ·nTiO <sub>2</sub> ·mH <sub>2</sub> O	
<b>Perovskite</b>	CaTiO <sub>3</sub>	
<b>Geikielite</b>	MgTiO <sub>3</sub>	
<b>Titanite or sphene</b>	CaTiSiO <sub>5</sub>	
<b>Titaniferous magnetite</b>	(Fe·Ti) <sub>2</sub> O <sub>3</sub>	

Rutile and anatase are produced industrially in large quantities. Brookite has no value for the pigment industry due to the difficulties in producing it. TiO<sub>2</sub> in the rutile form is the most important white pigment due to its light scattering properties, its chemical stability and lack of toxicity. About 4.2x10<sup>6</sup> tonnes of titanium dioxide was produced in 2003 [17-19].

Table 2 Properties of the different forms of titanium [20-23].

Property	Anatase	Brookite	Rutile
Melting point (°C)	350-1175 (Change to rutile)	500-600 (Change to rutile)	1830-1860 (in air)
Density (g/cm <sup>3</sup> )	3.90	4.13	4.27
Refractive index 5893 Å, 25°C	n <sub>ω</sub> = 2.56 n <sub>ε</sub> = 2.49	n <sub>α</sub> = 2.58 n <sub>β</sub> = 2.58 n <sub>γ</sub> = 2.70	n <sub>ω</sub> = 2.61 n <sub>ε</sub> = 2.90
Hardness (Mohs scale)	5.5-6.0	5.5-6.0	7.0-7.5

Titanium dioxide has a photocatalytic effect on, for example, nitrogen oxides and this property has been investigated using titanium dioxide on building blocks in urban environments that are heavily exposed to NO<sub>x</sub> from traffic [24].

Titanium dioxide is amphoteric and can react both with very weak base or acid characteristics [17, 19]. The chemical and thermal history determines the solubility of the  $\text{TiO}_2$ , for example a strongly roasted  $\text{TiO}_2$  is very stable chemically. Titanium dioxide will not react with most organic or inorganic reagents. It will only dissolve in concentrated sulphuric acid and in hydrofluoric acid. This fact makes an approach to recovery and recycling of  $\text{TiO}_2$  from paint by dissolution less interesting. However, it was briefly addressed in this work.

### **Titanium aqueous chemistry and leaching of titanium-containing material in the literature**

Titanium oxide is known for its low reactivity and solubility. Therefore the dissolution of titanium and titanium oxides has been studied rather extensively. The focus is mainly in three different areas: Production of titanium and titanium dioxide by hydrometallurgical methods from ores, from geological perspectives to study minerals and finally the leaching conditions of titanium in humanlike conditions. An overview of the work from several different authors can be found in Table 3. Leaching of ilmenite is a hot topic as the producers of titanium metal and titanium based pigments are turning to the more abundant ore, ilmenite, as a raw material. The problem with ilmenite is that the purity is too low for the chloride production process (see next chapter). Several proposed processes for upgrading the ilmenite to synthetic rutile, which is suited for the chloride process, are summarized in a review by Zhang et al. [4]. Note that pigments are usually pure titanium species of rutile and anatase, so it can be a bit risky to predict the leaching of titanium from paint waste from results based on studies on ilmenite.

Different authors have different views on the best method to leach titanium. This provides a lot of possible routes that can be explored, but is also an issue with no overall consensus. The most important conclusion is that strong acids are needed, together with elevated temperatures. Several authors also get better results in reducing conditions.

The precise titanium compounds in aqueous acid media remain somewhat debated. One of the main reasons for this is the difficulty to achieve thermodynamic equilibrium in aqueous systems containing titanium. It is thought that the main species of titanium in aqueous solution are  $\text{Ti}(\text{OH})^{3+}$ ,  $\text{Ti}(\text{OH})_2^{2+}$  or possibly  $\text{Ti}(\text{OH})_6^{-2}$ . In a strong acidic solution the main species is  $\text{TiO}^{2+}$  in equilibrium with  $\text{Ti}(\text{OH})_2^{2+}$  and  $\text{Ti}^{+4}(\text{aq})$ , but the existence of titanyl ion,  $\text{TiO}^{2+}$ , has never been proven and it is not determined whether it exists as  $\text{TiO}^{2+}$  or  $\text{Ti}(\text{OH})_2^{2+}$ . At higher pH the presence of species such as  $\text{Ti}_3\text{O}_4^{4+}$  yield colloidal or precipitated  $\text{TiO}_2 \cdot n\text{H}_2\text{O}$  [19, 25, 26]. The results of Nabivanets showed that titanium (IV) tends to form complexes in increasing order with  $\text{NO}_3^- < \text{Cl}^- < \text{SO}_4^{2-}$  [26].

Table 3 Overview of leaching studies on titanium containing material (L/S stands for liquid to solid ratio ; b.p stands for boiling point).

Reference	Raw Material	Type of Acid/Base	Acid/Base Concentration	Temp. range	Reducing agent	Other parameters and Notes
[27]	Ilmenite	HCl	7M-12M	Room temp to 100°C	Metallic iron	L/S, reaction time, grain size
[28]	Ilmenite	HCl	5M-10M	80°C-100°C	Metallic iron	L/S, reaction time, amount of Fe
[29]	Ilmenite	HCl	11M	30°C-80°C		
[30]	Ilmenite and Rutile	HCl or H <sub>2</sub> SO <sub>4</sub>	0.03M-1M	40°C-90°C		
[31]	Red Mud	H <sub>2</sub> SO <sub>4</sub>	0-18M	110°C		
[32]	Ilmenite	H <sub>2</sub> SO <sub>4</sub>	4.5-6M	85°C-100°C	SO <sub>2</sub> or Ti(III)	Particle size
[33]	Rutile	Various pH 1-13		100°C-300°C		
[34]	Ilmenite	KOH	21M-28M	180°C-100°C		Stirring. Particle size, L/S
[35]	Titanium Slag	NaOH	8M-10M	Room temp to 260°C		L/S, reaction time
[36]	Red Mud	H <sub>2</sub> SO <sub>4</sub>	1.5M-3M	40°C-60°C		L/S
[37]	Ilmenite	HF	1.3M-10M	30°C to b.p of HF		Reaction time, L/S, leaching stages
[38]	TiO <sub>2</sub> (anatase)	HF-HCl mix	HF 0.1-1.5M HCl 0.5M	37°C-95°C		Reaction time
[39]	Treated Ilmenite	HCl	6.5M	160°C		
[40]	Treated Ilmenite	HCl	1.6M-4.9M	30-75°C		
[41]	TiO <sub>2</sub> (anatase)	Organic acids	0-0.2M	Not specified		
[42]	Ash	Inorganic acids	Concentrated	25°C-95°C		
[43]	Red mud	H <sub>2</sub> SO <sub>4</sub>	1M-2M	60°C-90°C		Ultrasound enhances leaching

## Manufacturing of titanium dioxide pigment

The main minerals for titanium production are rutile, ilmenite and leucoxene. In 2009 ilmenite supplied 90% of the world's demand for titanium minerals and ilmenite will continue to be the major source for titanium [4]. The minerals anatase and perovskite are rich enough to have economic potential as titanium sources, but the high abundance of ilmenite and rutile has postponed the interest in other minerals [2].

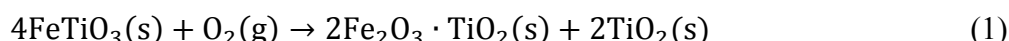
There are two processes for producing titanium dioxide pigment: the sulphate process and the chloride process. The sulphate process was the first one developed in 1916 but as the chloride process has advantages in both cost and waste management issues it is now the dominating process. However, China's extended production capacity in recent years has been realized using the sulphate method [1, 5]. Most new plants that are built outside China apply the chloride process route [23]. Rutile ore is not suited for the sulphate process as it does not readily dissolve in sulphuric acid, while the high iron content in ilmenite would produce a lot of ferric chloride waste in a chloride process [20]. With the sulphate process is it possible to produce both anatase and rutile crystals, while the chloride process only procures crystals in the form of rutile [44]. As the chloride process and the growing titanium metal industry rely on high grade rutile as a raw material the process of transforming ilmenite to synthetic rutile

has become very important. These upgrading processes are generally expensive multi-stage processes involving reductive conversions and leaching [4].

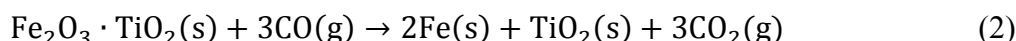
### **Upgrading ilmenite feedstock to synthetic rutile suitable for the chloride process**

There are several commercialized and proposed processes to produce a synthetic rutile that can be used in the chloride process. A process called the Becher process is usually used to represent the industrial process of upgrading ilmenite to synthetic rutile. Over four major steps the iron oxide is removed from the ilmenite and the product is a synthetic rutile containing over 90% TiO<sub>2</sub> [4].

The first step is oxidation of the ilmenite by heating the ore in a rotary kiln with air, to convert the iron to iron oxides



The pseudobrookite (Fe<sub>2</sub>O<sub>3</sub>·TiO<sub>2</sub>) is then reduced in a rotary kiln at >1200°C, in the presence of a mixture of coal and sulphur, to produce metallic iron [4]



Elemental sulphur can be added in the step above to capture manganese, which can then be removed in a subsequent leaching step. Borate flux may also be added to convert radionuclides, uranium and thorium to borate forms that also are more easily leachable [45].

The metallic iron is oxidized with air in a 1% ammonium chloride solution at 80°C for 12-16h to oxidize the iron which precipitates as iron oxides or hydroxides. The finer iron oxide particles are then separated from the larger particles of synthetic rutile [4, 45]



After the size separation the synthetic rutile is leached in 0.4wt% H<sub>2</sub>SO<sub>4</sub> to bring the TiO<sub>2</sub> content to about 93wt%. To this day the iron residue produced in this process (0.7 to 0.95 tonnes residue per tonne produced synthetic rutile) is returned to the mine site [4, 45].

### **Sulphate process**

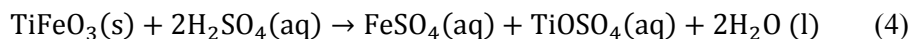
The first commercialized technology to produce titanium dioxide is a hydrometallurgical process named the sulphate process [4].

Ilmenite (40-60% TiO<sub>2</sub>) and/or titanium slag (72-87% TiO<sub>2</sub>) is turned into water soluble sulphates, titanyl sulphate TiOSO<sub>4</sub> and iron sulphates, by digestion in sulphuric acid over a few hours. By adding scrap iron the ferric iron is reduced to ferrous iron. After this the solution is cooled and the iron crystallises as ferrous sulphate heptahydrate, also known as copperas (FeSO<sub>4</sub>·7H<sub>2</sub>O) [4]. Through hydrolysis with steam the dissolved titanium is converted to a titanium oxyhydroxide precipitate (TiO(OH)<sub>2</sub>). The precipitate is washed, bleached with reducing agents and calcinated at about 1000°C to remove the water [4, 45, 46].

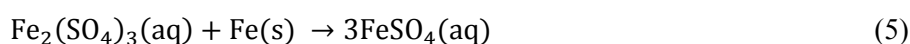
A simplified flow diagram can to be found in

Figure 4 and a typical sulphate process involves the following reactions [4, 46]:

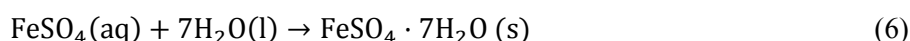
#### **Leaching/digestion**



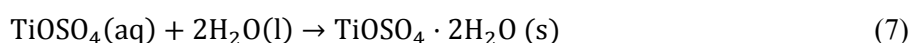
#### **Ferric reduction**



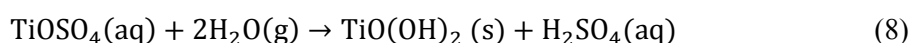
#### **Ferrous sulphate crystallization**



#### **Titanyl sulphate precipitation**



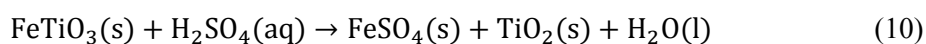
#### **Hydrolysis**



#### **Calcination**



#### **Overall reaction**



Waste is produced in large quantities in the form of iron sulphates, resulting in a higher production cost compared to the chloride process [4].

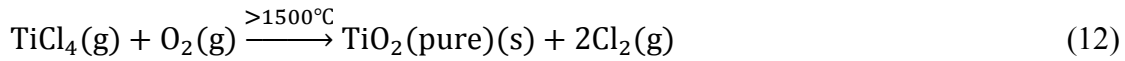
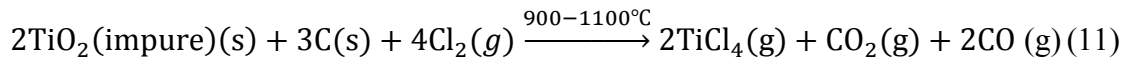
#### **Chloride process**

The chloride process is a thermo chemical process to produce a purer form of  $\text{TiO}_2$  or to produce titanium metal [4], see

Figure 4 for flow diagram. High  $\text{TiO}_2$  content in the feedstock is necessary to reduce the waste produced and to reduce productions costs [47].

The titanium feedstock is chlorinated to  $\text{TiCl}_4$  gas at 900-1100°C in a fluidised bed reactor. All impurities except silica are also turned into gaseous chlorides. The impurities are separated from the major product flow through condensation: The temperature is lowered to 200-250°C. At this temperature all chloride impurities condense but the titanium chloride stays in gas phase. After the separation step the temperature is decreased to below 0°C to turn the  $\text{TiCl}_4$  into a liquid. The liquid is then further purified through chemical treatment and distillation. The purified  $\text{TiCl}_4$  is oxidized at temperatures above 1500°C to give  $\text{TiO}_2$  and chloride gas. The chlorine is finally recycled back into the process [4, 16, 23].

General reactions are



To produce titanium metal the titanium dioxide is reduced to titanium sponge, which can be used to produce titanium metal. The most common process to produce titanium metal is the so called Kroll process where titanium tetrachloride is reduced with magnesium as the reducing agent [20]

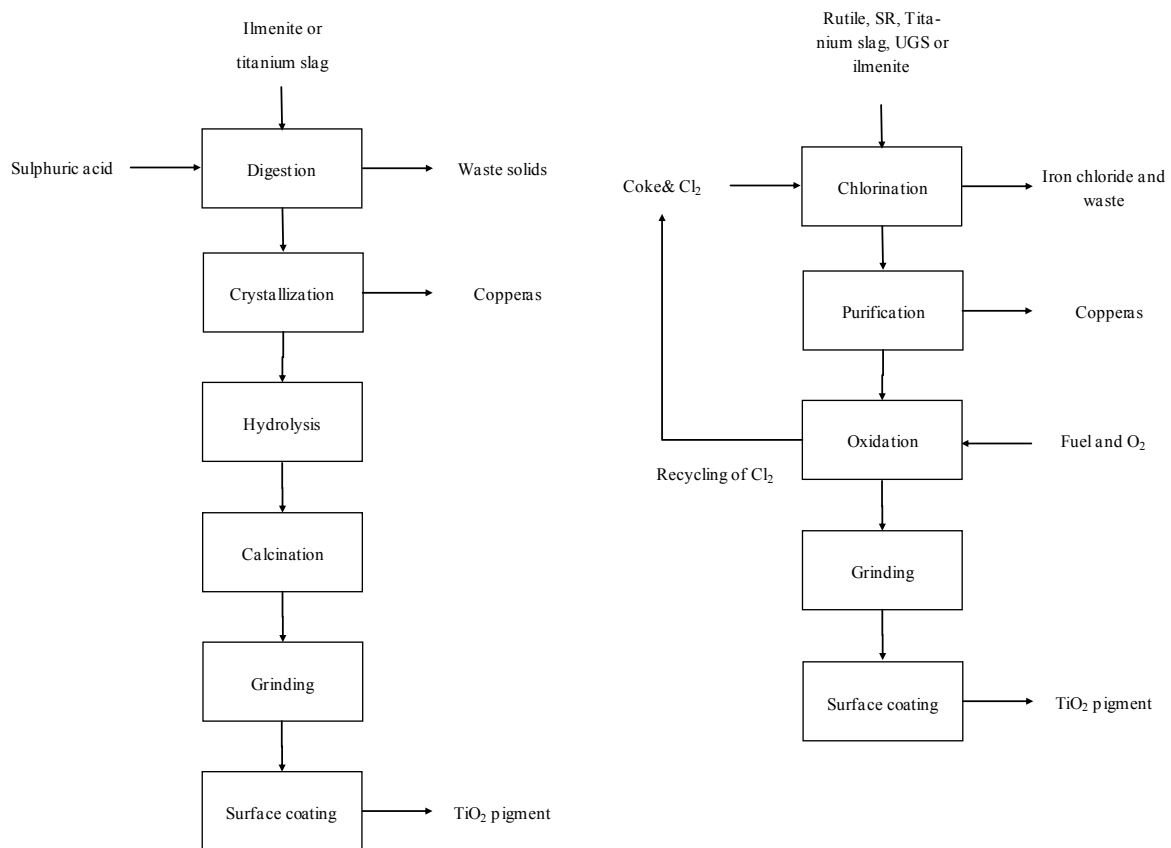


Figure 4 Simplified flow diagram of the sulphate process (to the left) and chloride process (to the right) [45].

### Post treatment

To optimize the TiO<sub>2</sub> performance as a pigment it is washed, filtered and milled to the right particle size and size distribution. Usually the pigment is given a surface treatment to optimize dispersibility, opacity, gloss et cetera. The surface treatment is chosen to fit the final pigment application [16].

## Titanium dioxide as a pigment

The most important quality of a white pigment is the ability to give the paint opacity and white colour to cover the substrate it is applied to. While several non-pigment uses exist for titanium dioxide, the most important use is as a white pigment in a wide range of products, for example, paint, plastics and paper. The pigment appears white due to its ability to scatter visible light. Titanium dioxide in the rutile form is however not perfectly white since it absorbs some of the light in the 400-500nm interval, thus giving more cream-toned whites. The anatase form absorbs less in this region, giving it a slightly bluer tone, but rutile is generally more preferred for its higher refractive index [18]. High whiteness requires a high level of chemical purity, especially the absence of transition metals and compounds thereof. The opacity of white pigments comes from the ability to scatter light. A high refractive index gives higher opacity. In the light scattering process the particle size of the  $\text{TiO}_2$  is also important. A particle size of circa 300 nm is the most suitable for the scattering of visible light and thus the particle size must be tightly controlled. Due to the opacifying properties of  $\text{TiO}_2$  it is used not only in white coatings but also in coloured paint systems as well [16, 48]. Titanium dioxide became commercially available in 1916 but it was not until the toxicity of the lead based pigments was understood in the 1950s that titanium dioxide became popular. By the 1970s titanium dioxide was the most used pigment in coating formulations [5]. Today titanium dioxide itself accounts for roughly 70% of the total volume of all used pigments combined [3].

The two forms of titanium dioxide used commercially in paint, rutile and anatase, differ in how the titanium and oxygen are arranged in the crystals lattices, see Figure 5. This gives differences in refractive indices, densities and UV reactivity. The higher refractive index of rutile compared to that of anatase comes from the longer distance in the Ti-O binding in rutile (anatase:  $1.937 \pm 0.003 \text{ \AA}$  and  $1.964 \pm 0.009 \text{ \AA}$ ; rutile:  $1.946 \pm 0.003 \text{ \AA}$  and  $1.984 \pm 0.004 \text{ \AA}$ ). The rutile crystals are stubby needles with higher density and refractive indices while anatase is thick platelets. Rutile is the most stable phase, with a melting temperature of roughly  $1850^\circ\text{C}$  in atmospheric pressured air and anatase will undergo a phase conversion to rutile at temperatures between  $350\text{-}1175^\circ\text{C}$ , see Table 2 [17-19].

As mentioned previously,  $\text{TiO}_2$  functions as a UV-energized oxidation catalyst. It is active as such a catalyst, not only for decomposition of nitrogen oxides, but also for oxidation of organic polymers, which is important for paint applications. The surface of an anatase particle is 10 times more reactive than the same surface of a rutile particle and it takes only 10 percent contamination of anatase in rutile to reduce the life expectancy of a polymer in a paint film by half. This means that for all outdoor applications a high purity rutile pigment is essential [49].



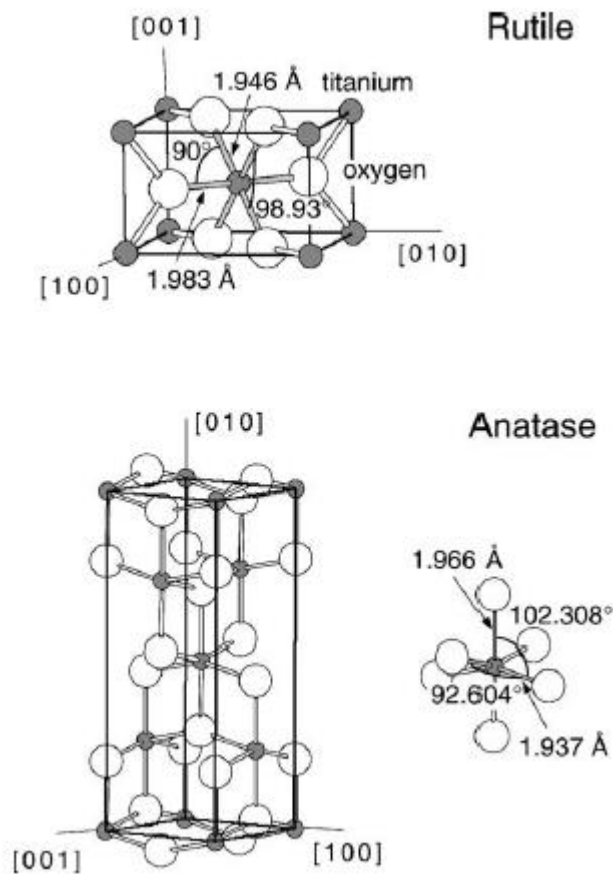


Figure 5 Rutile and anatase crystal cells with length and angles between titanium and oxygen. Rutile is tetragonal with  $a = b = 4.587 \text{ \AA}$  and  $c = 2.953 \text{ \AA}$ . Anatase is tetragonal with  $a = b = 3.782 \text{ \AA}$  and  $c = 9.502 \text{ \AA}$  [50].

## Composition and surface of the pigments

Commercial pigments are designed to meet specific requirements for specific customers.  $\text{TiO}_2$  is often named as the major white pigment due to its good properties but commercial pigment grade  $\text{TiO}_2$  is often not 100% pure. The crystallite core is the active ingredient that provides the optical functions. The surfaces of the core  $\text{TiO}_2$  particle do not only consist of titanium and oxygen. As the  $\text{TiO}_2$  crystals grow during manufacturing insoluble components accumulate on their surfaces. These components are either impurities from the ore or additives deliberately used to control crystal structure, crystal growth and particle agglomeration. The layers of these “non- $\text{TiO}_2$ ” molecules are only a few molecules thick. Important deliberate surface treatments are coatings of inorganic and organic substances essential for the dispersion and the durability of the pigment [49, 51].

Commercial  $\text{TiO}_2$  pigments can be divided into three groups [49]:

- Uncoated pigments
- Coated pigments
- Slurries

### **Uncoated pigments**

Uncoated pigment qualities usually contain at least 98wt%  $\text{TiO}_2$ . Some elements from the ore or the manufacturing process can affect pigment performance. Trace contaminations are usually unimportant, except for compounds of transition metals such as iron, chromium and vanadium, as these affect the colour of the pigment [49].

Titanium dioxide pigments produced by the sulphate process contain up to 0.3wt% niobium and 0.3wt% phosphorus from the ore, calculated as the respective pentoxides. Some alumina (0.2wt%) can be added to compensate for pentavalent impurities, thus minimizing their contribution to discoloration [49].

There are usually no unwanted impurities from the ore in the pigments produced by the chloride process. About 1%  $\text{AlCl}_3$  and low concentrations of other metal ions are usually added to the  $\text{TiCl}_4$  stream before oxidation for better process control and to improve photochemical stability of the pigment. Most of these metal species will concentrate at the surfaces of the titanium dioxide crystals. Titanium dioxide pigments from the chloride process with a surface coating of aluminium species have the advantages of being nearly anhydrous, which gives benefits in certain plastic applications where hydrous components cause bubbles and holes in extruded films [49].

Both uncoated and coated pigments can contain some organic polyhydroxyl compounds. These are remains from decomposed grinding aids used to improve the dry flow characteristics during the milling of the pigment. Unmodified pigments tend to cake and flow poorly and silicones would be even better alternatives as additives to improve the flow characteristics but this would make the pigment hydrophobic, and therefore unsuitable for most coating applications [49].

### **Coated pigments**

Most surface treatment methods and additives used are well-guarded manufacturing secrets. It can be assumed that most surface treatments are done either to obtain better stability of the dispersed pigments in their media, or to reduce the grinding time needed to break down the number of agglomerates to an acceptable level, or to reduce the photo activity of a pigment [51, 52].

Both anatase and rutile absorb ultraviolet light. This energy mainly dissipates as heat but can give rise to electronically excited species at the pigment surface that can oxidise organic molecules absorbed on, or close to, the pigment. These processes catalyse the degradation of the paint film. The high photo activity of anatase makes it unusable in exterior applications and it was not until the late 1940s, when the surface treated rutile grades reached the market, that titanium dioxide could be used successfully outdoors. Untreated rutile can absorb ultraviolet light and this protects the deeper layers of the paint film, but the photo-catalysed oxidation of the paint film will contribute to a rapid degradation of the film [52].

Typical  $\text{TiO}_2$  pigments can be coated with hydrous aluminium oxide particles. This lowers the van der Waals forces between the pigment particles, thus decreasing particle-particle attractions. The alumina coating makes the pigments dispersible with conventional pigment

equipment. Nondurable grades of pigments contain up to 5% hydrous alumina. Durable grades have an additional coating of 2 to 8wt% silica. For maximum weather stability a coated pigment can contain 7 to 10wt% of, for example alumina, zirconium and tin oxides or phosphates and silica [49, 52].

Silica coated pigments come in two different modifications; either “fluffy” or “dense”. “Fluffy” silica is porous sub-microscopic particles of silicic acid. The surface coating using this kind of silica is done to give a controlled distance between pigments and maximize the number of air-pigment interfaces, thus improving the dry-hiding property of high pigment volume concentration (PVC) paints. This kind of silica coating also tends to reduce paint gloss. Pigments for high solid dry-flat hiding paints contain 5 to 10wt% hydrous silica and 3 to 6wt% hydrous alumina [49, 52].

“Dense” silica is used for super durable pigments in which each individual pigment particle is encapsulated in a glassy silica shell. The end product for these pigments is normally car coatings [49].

The pigments can also be treated with an organic coating to make the pigment even easier to incorporate into the paint media. The organic coating enhances the dispersibility of the pigment and makes it less prone to agglomerate during storage. Polyhydroxy compounds such as polyalcohols and tertiary amines are commonly used. Pigments for plastic and other non-polar media can be surface-treated with silicon oils to reduce the hydrophilicity of the pigment [52].

### **Slurries**

Pigments in an aqueous dispersion are called pigment slurries. Normally the dispersion of the pigment is done by the pigment consumer but sometimes slurries can be provided by the pigment producers. Slurries normally contain up to 80wt% coated pigments. To stabilize the dispersion and to avoid flocculation of the pigments carboxylic acid dispersants are added. Some type of pH modifier, such as an amine, is normally also used and biocides are added to inhibit microbiological growth. Altogether roughly 1% of organic material is normally present [49].

### **Basic paint chemistry**

There are many different characteristics that are desirable for paint formulations, for example high opacity, a certain gloss and texture, good chemical resistance, durability, resistance to mechanical wear and good adhesion to the substrate. It is naturally highly challenging to make formulations with all of these desired qualities [53]. Paint formulations are therefore usually very complex and contain many different components but generally paints can be divided into four major parts: binder, solvents, additives and pigments [54]. The use of major raw materials in the paint industry is shown in Table 4. Note that in this thesis the extenders will be classified as pigments and as white paint is the focus of this work organic pigments will not be discussed.

Table 4 Raw materials used by the paint manufacturing industry in general in 1982 (both industrial and decorative) [55].

Material	Usage in percent of total type of material
<b>Binder</b>	
Alkyd	33%
Acrylic	19%
Vinyl	19%
Other	29%
<b>Pigments</b>	
Titanium dioxide	65%
Inorganic	33%
Organic	2%
<b>Extenders</b>	
Calcium Carbonate	31%
Talc	25%
Clay	23%
Other	21%

### Binder

The binder, also known as the film-former, is the component that normally identifies the paint, for example alkyd paint or emulsion paint. It is the part of the paint formulation that forms the dry paint film on the substrate. Without the binder holding the dry pigments in place the paint or coating would be very susceptible to wear. A varnish, which is absent of pigments, still protects the surface and gives a decoration effect called gloss or “sheen”. There are several types of binders, such as linseed oil, polyesters, epoxies and urethanes, of which alkyd and so called emulsion paints are the most common types in decorative paints [54, 56, 57].

### Solvent

To facilitate the application of the paint or coating on the substrate the paint needs to be fluid. The term “solvent” is used in paint contexts to describe any liquid that is present in, or added to, a paint formulation. The term “solvent” can be somewhat misleading as it does not say anything about the ability to solve any of the paint components and the term diluent is more correct but less used. In modern decorative emulsion paints the most common solvent is water [56].

### Additives

Paint formulations are complex mixes of inorganic and organic components, which can be difficult to mix together into a homogenous product. Additives are commonly added to a paint formulation to overcome these shortcomings and to tailor make the final product for certain applications. Examples of common additives are viscosity modifiers, anti-foaming agents, surfactants, and biocides. They are normally added in small amounts (roughly from 0.001wt% and rarely more than 5wt%) but have a large impact on the properties of the final product [56, 57].

## Pigments and extenders

There is a vast variety of inorganic pigments and extenders with their own specific chemical composition, crystal structure and so forth used in paints and coatings. Table 5 lists some of the different inorganic components that can be found in a paint waste stream. The additions of pigments to a coating formulation basically provide two different kinds of benefits, namely decorative and protective effects [56].

Mineral pigments, or extenders or fillers, have traditionally been used to dilute a more expensive product without compromising on the desired qualities. The characteristic of a filler that does not affect the properties of the paint is that it should reduce the total cost of the whole product, be chemically inert and have the correct particle size. Nowadays almost all extenders can be seen as functional fillers with their own purpose and function in a coating formulation. They are still used to add bulk to the system for financial gain, but the choice of filler is based on its physical and chemical characteristics and how it will affect the whole coating system. The carbonates are probably the most widely used extenders based on weight consumed. This group includes calcium carbonates derived from chalk, white crystalline limestone, marble, aragonite and chemically precipitated calcium carbonate (PCC) as well as dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ). The major advantage with carbonates is their abundance. Having a source of the mineral in close vicinity to the paint manufacturing facility is normally the major reason for using these minerals and quality can be compromised if high quality material is not available within a nearby distance. The consequence of this is also that the carbonates can be replaced with another extender that is more abundant in the area. This gives large variations in coating formulations depending on which extenders are available locally. Common complements/replacements for carbonates are kaolin (kaolinite) and talc [18].

Many extenders are more or less untreated minerals but there are also synthetically produced extenders that have the advantages of having a narrower particle size distribution and higher chemical purity. Examples of synthetic extenders are synthetic calcite or aragonite crystals called precipitated calcium carbonate (PPC) and a barium sulphate called blanc fixe [18, 58].

Table 5 Different kinds of extenders that are used in paint and coatings [18, 58] (Note: chemical compositions given are only theoretical. Most extenders come from natural minerals and contain minor impurities).

Extender	Mineral example	Theoretical composition
Carbonates	Calcite, Aragonite, Dolomite	$\text{CaCO}_3$ , $\text{MgCO}_3$ or $\text{CaMg}(\text{CO}_3)_2$
Kaolin	Kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
Talc		$\text{Mg}_6[\text{Si}_8\text{O}_{20}](\text{OH})_4$
Silica	Perlite, Diatomite, Tripoli, Novaculite	$\text{SiO}_2$
Barytes		$\text{BaSO}_4$
Nepheline		$\text{K}_2\text{O} \cdot 3\text{Na}_2\text{O} \cdot 4.5\text{Al}_2\text{O}_3 \cdot 20\text{SiO}_2$
Mica	Muscovite	$\text{Al}_3\text{KSi}_3\text{H}_2\text{O}_{12}$
Wallastonite		$\text{CaSiO}_3$

### Important pigment qualities

To summarise the sections on different components used in paints above one can conclude that all of these components affect the properties of the paint. A systematic approach to evaluating the effect of each component is very time consuming and costly. Thus, one common way of evaluating a new paint component is to incorporate it into a coating formulation and evaluate the properties of the final product. However, there are some pigment properties that are commonly measured due to their great importance.

Opacity and colour are two very important characteristics of a paint film. The opacity of paint is defined as the ability to hide the painted substrate. To hide the substrate the pigment has to hinder the light from passing through the paint film, reaching the substrate and bouncing back to the observer's eye. The ability of a pigment to obliterate the substrate is dependent on its ability to either scatter or absorb light [59]. Coloured pigments absorb the incoming light while white pigments reflect the light. In most cases a combination of scattering and absorbing pigments gives the best opacity [53].

The absorbing and scattering capability of a pigment depends on the wavelength of the incoming light, on the pigment's crystal structure, the refractive index and the particle shape and size. The ability of a pigment to scatter light increases with particle size until it reaches a maximum, then the scattering ability decreases as particle size continues to increase. As a guideline can it be said that the particle size should be half of the wavelength it is should be able to scatter. Visible light has a wavelength of 360 nm to 780 nm so normal pigment sizes lie in the range of 0.1 to 10  $\mu\text{m}$ .

Extender pigments, such as calcium carbonates and clay minerals typically have refractive indices in the range of 1.4-1.6. White pigments with refractive indexes of 2.0-2.7 are used to improve the hiding power of coatings. Titanium dioxide is the main white pigment due to its high refractive index and its low absorption of light in the visible spectrum. Thus, white paints with high opacity can be made of paints based on titanium dioxide. Examples of refractive indices of some media, as well as for minerals used in paint are shown in Table 6 [53, 60].

Table 6 Refractive indices of some common paint components [53].

Media	Refractive index	Pigment/Extender	Refractive index
Air	1.0	Calcium Carbonate	1.58
		Kaolin/China Clay	1.56
		Talc	1.55
Water	1.33	Baryte (Barium Sulphate)	1.64
		Zinc Oxide	2.01
		Zinc Sulphate	2.37
Film formers/Binders	1.4-1.6	Anatase	2.55
		Rutile	2.76

The colour of an inorganic pigment is determined by its crystal structure and can be affected by impurities, physical stresses and temperature. The colour of the light reflected from a painted surface is a combination of the colours of the substrate, the pigment used and the dispersion media of the coating. In most cases the media does not contribute to the colour and when the substrate is completely hidden the determining factor for the colour of the coating is the colour of the pigment. Unabsorbed light passes through the pigment and is eventually refracted to the eye. Depending of which wavelengths of light are refracted back different colours are perceived [59].

The shape of the pigment particles has a significant impact on the properties of a paint film. For example, rod-shaped particles can reinforce a film, much like iron bars in concrete, or poke out through the surface and reduce gloss. Another example is plate-like particles, which tend to overlap each other and give the coating a resistance against water penetrating through the film [56].

The surface area of a particle depends on the particle size and morphology. As the pigment particles are very small, the surface characteristics of the pigments will have a profound impact on the properties of the whole paint [49]. The surface area of the pigment often gives an indication of the opacity it can create, since most of the scattering and absorption of light occurs on the particle surfaces. The total available surface area is also an important value for the calculation of an approximate dispersant demand in cases when a dispersant is used to keep the pigments de-agglomerated in the paint and on rheological properties of the pigment [59].

### **Paint manufacturing**

One of the most crucial steps in paint manufacturing is to make a stabile dispersion of the pigments [53]. As mentioned before, the particle size is important for achieving the maximum light scattering per weight unit of pigment. In the pigment production process the pigments are normally grown into a suitable crystal size, but pigments tend to aggregate during transport and storage. This means that grinding to break up agglomerates is a vital part of manufacturing in paint production [49].

The first step in paint manufacturing is to produce a so called mill base in which the pigments are dispersed [53]. The main components of the mill base are inorganic pigments, part of the dispersion media, for example water or the binder, and possible surfactants, rheology modifiers and other kinds of additives [56]. The dispersion of the pigments can be described as a three step process: wetting of the pigments with the dispersion media, the breaking up of pigment aggregates with high shear forces and finally the stabilization of the single or slightly flocculated pigment particles [53, 56, 61]. The main goal of the dispersion of the pigments is to break down particle assemblages to make a homogenous dispersion where the particles are evenly distributed in the media. When this is done the rest of the carrier liquid, binder and all other additives are added and everything is mixed to produce the final paint product [53, 61].

### ***The role of surfactants and surface chemistry in paint manufacturing***

The final mixing stage in paint production is a rather straightforward process where the different components are mixed together. On the other hand the dispersion process, with its different steps (wetting, grinding and stabilization), is a rather complicated physical and chemical process. In all these steps the forces between particle surfaces play a major part. Properties such as isoelectric point, dispersion ability and aggregation are all surface-dependent [62, 63].

The polarity of the molecules in the dispersion medium and at the pigment surface is very important in the wetting process. Surfactants are commonly added to lower the interfacial tension between the solid pigment and the carrier liquid. The addition of surfactants enables improvement of the wetting of the pigment, the dispersibility and the stability of the dispersion. The choice of surfactant depends on the pigment and the paint system. For example it has been documented that a sodium salt of carboxylic acid will have a promoting effect on the dispersibility of titanium dioxide pigment but will have the opposite effect on carbon black pigment [53]. Non-ionic and anionic surfactants are commonly used in the pigment industry. Ammonia or amine polyacrylate salts are commonly recommended as these compounds can escape the paint film as it dries while sodium and potassium groups stay in the dried paint film and reduce the durability against water [64].

To keep the pigment particles dispersed a repulsive force (in the form of electrical or steric forces) has to overcome the attractive van der Waals forces. Charge/electrical stabilization occurs when the particles have the same surface charge and thus repel each other if they come too close. Steric or entropic stabilization is obtained and then a dispersion agent is adsorbed on the surface of the pigment and the tail of the dispersion agent is solvated in the dispersion media and such creates steric barriers which hinder the dispersed particles from colliding and attracting each other [61].

These surfactants can either be attached at the surface before the dispersion process (as a surface treatment of the pigment) or during the dispersion process (as a dispersing agent). Note that high concentration electrolyte dispersant can increase the ion concentration of the liquid and thus reduce the stability of the dispersion [62]. Steric stabilization is not as important in aqueous systems where the electric double layer reaches out further than the steric barriers of the polymers. An exception to this is when the ion strength is high [65].

As pH affects the surface charge the pH also affects the stability of a dispersion. For a certain combination of pigment, dispersion agent and ion concentration there is a pH which gives the pigment surface a zero charge. This pH is the so called isoelectrical point. Above this point the net charge of the surface is negative and below this point the net charge is positive. The stability of dispersion is at a minimum at plus/minus one pH unit around the isoelectrical point. Paints normally contain a mixture of different pigments and extenders with different isoelectrical points. This complicates the charge stabilization as the different pigments will have different charge at different pH [64].



## Pyrolysis

Pyrolysis is a thermal process for degradation of organic materials in the absence of air into carbonaceous char, oils and combustible gases at a relatively low temperature (400-800°C). Pyrolysis is also known as carbonization, destructive distillation, dry distillation or retorting. The major differences between combustion and pyrolysis are the heat generation/demand and the products of the processes. Combustion is an exothermic reaction while pyrolysis is endothermic. The combustion products are carbon dioxide, water and ash while a pyrolysis process generates char, oil or tar in addition to various gases [66, 67]. By adjusting the heating rate and the maximum temperature the ratio between char, oil and gas can be modified [67]. Faster heating and higher maximum temperatures generally produce higher ratios of oil and gas compared to char and as the residence time in the furnace increases the yield of the liquid phase decreases and more gas is produced [67, 68]. The chemical composition of the oil is dependent on the feedstock and the process parameters. The gas phase mainly consists of carbon dioxide, carbon monoxide, hydrogen, methane and other hydrocarbon gases and uncondensed pyrolysis oils [67]. Both the oil and the gas can potentially be utilised as fuels or as feedstock for chemical syntheses.

The heating can be provided by conventional heating, for example internal (by partial combustion of fuel) or external heat sources of the reaction or electrical resistance, or by microwave heating. Microwave induced pyrolysis of a number of waste types, such as sewage sludge [69], car tires [68], plastic wastes [70] has been described in literature. Differences between conventional and microwave heating are presented in Table 7.

Table 7 Differences between conventional and microwave heating [68].

<b>Conventional heating</b>	<b>Microwave heating</b>
Long reaction time (hours)	Short reaction time (minutes)
Slow transfer of heat, thermal conductivity of polymer is low	Easier heating of polymers
Low heating efficiency	High heating efficiency
Every fuel source may be employed	Electrical power is required
Additive not required	Microwave absorber are required

Compared to conventional heating with an external heat source the heat generated by microwaves is generated volumetrically within the exposed material. This gives the potential of a very uniform heating process. But this requires a uniform material, as different materials absorb microwaves differently [71]. A material can either be transparent to microwaves (low dielectric loss materials), an opaque material which reflects microwaves (no penetration) or an absorbing material (high dielectric loss) [72]. For example, carbon in the form of charcoal is very active while calcium carbonate, silica oxide, dolomite, muscovite, quartz and rutile are more or less transparent for microwaves with a frequency of 2.45 GHz, the most common frequency for industrial scale microwave heaters [73, 74]. The main advantage of microwave-assisted heating is the effective heating of composites consisting of mixtures of these different materials [72]. However, some problems can occur in microwave heating, such as so called hotspots where the material is exposed to a higher energy due to standing waves. [71, 74]

## Experimental

### Materials

Titanium dioxide (rutile) and some common extender pigments were acquired. The extenders chosen for this study were dolomite, kaolin, talc and mica. Unless otherwise stated, the pigments were used as delivered from Akzo Nobel Decorative Paint.

A model paint containing all the pigments/extenders was produced according to the formulation shown in Table 8. Equipment for mixing and paint preparation in the laboratory of Akzo Decorative Paints in Slough, United Kingdom was used.

Table 8 Composition of sample used in pyrolysis experiments in weight percent of total formulation. The components are divided into the four paint component groups presented in the Background section. The weight percent of pigments within themselves is also given.

Type of component	Component	Wt% Total formulation	Wt% only pigments
<b>Solvent</b>	Water	32.0%	
	Surfactants	0.7%	
	Coalescent aid	0.6%	
	Biocide	0.2%	
<b>Additive</b>	Organic polymeric hiding additive	5.0%	
	pH modifier	0.1%	
	Cellulosic rheology modifier	0.7%	
	Rheology modifier	0.2%	
<b>Binder</b>	Acrylic copolymer dispersion	33.6%	
<b>Pigment</b>	Dolomite	11.1%	41.3%
	Kaolin	1.2%	4.5%
	Talc	1.2%	4.6%
	Mica	1.2%	4.3%
	Rutile	12.1%	45.2%

In addition, a mixed pigment sample corresponding to the pigment composition in the model paint was prepared by mixing dry pigments together, see Table 8.

Two types of binders were also acquired, a vinyl acrylic latex copolymer with acrylic latex and a pure acrylic latex binder. These two binders were assumed to correspond to the major types of binders that can be found in paint waste. Both contain 52 weight percent polymer and 48 weight percent water.

A non-pigment quality of rutile (particle size  $<5\ \mu\text{m}$ , purity  $\geq 99.9\%$ ) to be used for comparison with pigment quality rutile was acquired from Sigma Aldrich. This rutile had no surface coating and was used to assess if the recovery process has an effect on the rutile itself or the surface coating of the pigment.

Concentrated nitric acid (64-66%, of puriss purity, Sigma-Aldrich), concentrated hydrochloric acid (37%, of puriss purity, Sigma-Aldrich), concentrated sulphuric acid (95-97%, of puriss purity, Sigma-Aldrich) and concentrated perchloric acid (70-72%, pro analyse, Merck) were used for leaching. All dilutions were made with MilliQ water ( $>18\text{M}\Omega/\text{cm}$ ). 1M nitric acid

that was used for dilution of ICP samples was prepared from concentrated nitric acid (65%, suprapur, Merck) and MilliQ water.

## Methods

### Leaching of pigments: Prestudy for hydrometallurgical recycling process

A leaching study of titanium dioxide pigment quality, rutile, was performed. The aim of the study was to investigate the plausibility of a hydrometallurgical route for the recovery of titanium from paint waste. The major process steps in this recovery route would consist of a leaching step followed by a separation of the aqueous titanium from other metal ions with solvent extraction.

Prior to leaching the pigment was dried at 125°C for 20 h plus/minus 30 minutes. The leaching was done in 100 ml plastic (PEHD) containers with different pure mixtures of concentrated acids, respectively. The acids used were pure concentrated H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub> and two mixtures of concentrated acids consisting of 25 volume percent HNO<sub>3</sub> plus 75 volume percent HCl, respectively, and mixtures each of 50 volume percent of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>. The solid to liquid ratio was 20 (20 ml acid and 1.0 g TiO<sub>2</sub>), stirring was done with a magnetic stirring bar (length 45 mm) and a speed of 175 rpm, leaching time 20 h and the leaching was carried out at 22-24°C. After evaluation of the results from the first experimental series it could be stated that leaching with HCl was better than the other acid mixtures. Based on these conclusions additional leaching was done with perchloric acid at different concentrations, namely 0.01 M, 0.1 M, 0.5 M 1.0 M and 4.1 M. The leaching was done with the same experimental conditions except with an increased stirring speed (375 rpm) and leaching time (7 days). All the samples were made in duplicate.

The samples were centrifuged at 14,000 rpm for 20 minutes after the end of the leaching time and samples of 1 and 0.1 ml, respectively, were taken from the supernatant liquid and diluted 10 or 100 times, respectively, with 1 M suprapur nitric acid. The samples were then analysed with Inductive Coupled Plasma Optical Emission Spectrophotometer (ICP-OES, Thermo iCAP-6000). An internal standard of 10 ppm Indium was added to all the samples to compensate for fluctuations in instrument response. External standards with concentrations of 0 ppm, 0.1 ppm, 1 ppm, 10 ppm and 50 ppm were used to create a calibration for determination of the concentrations in the samples.

### Characterisation of pigments and inorganic recovery residues with X-ray powder diffraction (XRD)

The main crystalline compounds in pigment samples were identified by qualitative X-ray powder diffractometry (XRD) using a Siemens D5000 X-ray powder diffractometer with the characteristic Cu radiation and a scintillation detector. Scan parameters used were: 2 $\Theta$ / $\Theta$  locked - Start: 10.000 ° - End: 70.000 ° - Step: 0.050 ° - Step time: 1. S.  $\Theta$  is the angle between the specimen surface and the X-ray beam. The identification of compounds was performed through comparison with standards in the Joint Committee of Powder Diffraction Standards [Joint Committee of Powder Diffraction Standards, JCPDS-ICCD: PDF-4 release 2013 Philadelphia, USA].

### **Thermo gravimetric analysis (TGA) and Differential scanning calorimetry (DSC)**

Thermo gravimetric analysis (TGA) was used to evaluate the heat stability of the major paint components. For detailed evaluation of the kinetics of the thermal reactions different parameter such as particle size, sample size and compaction and heating rate must be taken in account [75, 76]. Results presented in this work can provide a guideline for the thermal stability of the components but should not be viewed as a fully comprehensive study.

#### ***Heat stability of pigments***

Thermo gravimetric analysis (TGA) was used to evaluate the titanium dioxide and the extenders in the model paint. The data from the TGA experiments were used as guidelines for the maximum temperature for the pyrolysis process to avoid degradation of any of the pigments. A non-pigment quality of rutile was also measured as a reference for the titanium dioxide pigment. Results presented in this work can provide a guideline for the thermal stability of the components but should not be viewed as a fully comprehensive study.

A nitrogen atmosphere was used to simulate the oxygen free atmosphere in pyrolysis. All the pigments were measured on a NETZSCH STA 409 PC Luxx instrument and the non-pigment rutile was measured on a TA Instruments Q500. The measurement was from room temperature up to 1000°C with a heating rate of 10°C/min. Before starting an experiment the furnace was evacuated twice and then filled with N<sub>2</sub>.

#### ***Heat stability of binders***

The heat stability of two binder samples, a vinyl acrylic latex copolymer with acrylic latex and a pure acrylic latex (see material section for more info), was investigated using TGA. As the binder comprises the major organic component in paint the decomposition temperature of the binders were used as a guideline for the minimum pyrolysis temperature to be used in the proposed recycling process.

The samples were analysed on a TGA Q500 from TA Instruments with a heating rate of 5°C per minute. Both inert atmosphere (N<sub>2</sub>) and synthetic air (a mixture of 20% O<sub>2</sub> and 80% N<sub>2</sub>) was used in the TGA experiments. The inert atmosphere simulates pyrolysis conditions and synthetic air was used as comparison.

### **Surface area measurements**

The Brunauer–Emmett–Teller (BET) method [77] was used to measure the specific surface area of the powder samples. This was determined by N<sub>2</sub> adsorption, isothermal at 77 K using a Micromeritics ASAP2020.

Before measurement the samples were degassed at 60°C under high vacuum (roughly 1 µm Hg) until the samples were considered dry, or for maximum of 1500 minutes. The samples were considered dry when the measured pressured change due to the sample was lower than 5 µmHg/min.

The surface area cannot alone explain predicted characteristics such as dispersibility or hiding power of a pigment in a paint formulation [78] but in the present work BET measurements were used to compare the pigments before and after different processes. The degassing

temperature has a significant effect on the BET result [78] so a relatively low degassing temperature was chosen, which was assumed not to alter the surface of the pigment.

### Microwave pyrolysis experiments

The pyrolysis experiments were carried out in a pilot scale microwave pyrolysis furnace provided by Stena Metall AB, Göteborg. The dimensions of the pyrolysis chamber were 390 x 430 x 950 (mm) and the oven had a total capacity of 10 L [79]. The microwaves were produced by three magnetrons of model Samsung OM 75P with a fixed frequency at 2465 MHz [79] and an individual power output for each magnetron of 1.5 kW.

If not otherwise stated, all the magnetrons were running at full effect for a total power output of 1.5kW during the pyrolysis experiments.

The sample was placed in a container made of mica (transparent to microwaves) and weighed. Then the sample was placed in the pyrolysis furnace and the system was flushed with nitrogen gas before the heating started. The liquid residue fraction was continuously collected during the experiment but the gas fraction was not collected. All temperatures were measured continuously at three points, inside the sample, at the surface of the reaction vessel and in the gas outflow from the furnace, see Figure 6.

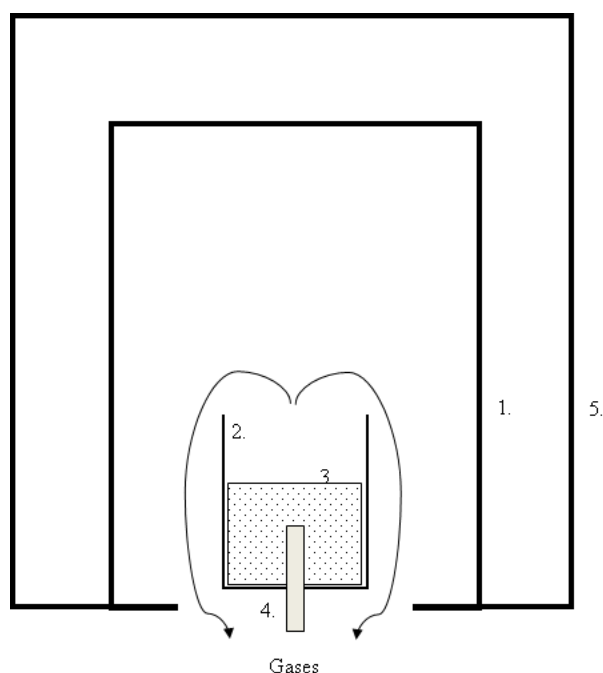


Figure 6 Schematic diagram of the pyrolysis reactor used in the pyrolysis experiments 1. Reaction vessel; 2. Sample crucible; 3. Sample ; 4. Thermocouple inside sample 5. Outer casing, continuously supplied with nitrogen gas.

After the experiment the dry residue and the liquid oil fraction were weighed and saved for analysis. The amount of gas produced was estimated by subtraction of the dry and liquid residue fractions from the total weight prior to the experiments. In the present work the focus was on the inorganic parts of the sample materials and therefore the oil and gas fractions were not analysed further.

Four pyrolysis experiments were made; three on the paint formulation described in Table 8 and one on the same formulation as previously but which had been dried prior to the pyrolysis experiment. Experiments 1 (wet paint) and 4 (dry paint) were designed for the initial evaluation of microwave pyrolysis as a method to recover the inorganic components from a waste paint. Experiments 2 and 3 were made on larger amounts of material in order to produce enough recycled pigment material to make it possible to manufacture a test paint based on a significant fraction of recycled pigments.

#### **After-treatment and characterisation of ash from pyrolysis experiment 1**

A large part of the solid residue from pyrolysis experiment 1 was taken (76% of the total sample) and ground to a homogenous powder for evaluation with XRD. The same homogenised sample was weighed, placed in a furnace and heated from 22°C to 400°C. The temperature was then held at 400°C for 230 min. After cooling the sample was weighed and analysed with XRD for comparison with the non-heat treated sample.

In addition, the effect of the after-treatment on the colour of the pyrolysed material was visually evaluated. This was done by placing samples of virgin rutile pigment, virgin dolomite, virgin mica, a mix of virgin pigments corresponding to the one in the pyrolysis ash, ground pyrolysis ash and heat-treated pyrolysis ash next to each other on a white background and visually comparing the whiteness of each sample.

#### **After-treatment and characterisation of ash from pyrolysis experiments 2 and 3**

The solid residues from experiments 2 and 3 were ground and mixed together. This material was then divided into 10 sub-samples which were heat-treated at 450°C in air for 3 hours. The weights before and after the heat treatments were recorded. After the heat treatment all the sub-samples were mixed together again to one sample and this material was analysed with XRD.

The specific surface area according to the BET-method was measured on the sample of pyrolysis ash before and after the extra heat treatment. The same measurement was made on a pigment mix corresponding to the pigments used in the pyrolysed paint and all the individual pigments (see Table 8) plus a non pigment quality of rutile. In addition BET was also measured on the same individual pigments after heating at 450°C in air for 3 hours. The weight changes after this thermal treatment of the pigments were also noted. The measurements on the mixed pyrolysis residues before and after heat treatment and a mix of pigments corresponding to the pigment mix in the pyrolysed paint were all measured in triplicates. This was done to get an understanding of the errors associated with the uncertainty of the BET measurement method. These samples all represent potential inhomogeneous samples that could give large differences between measurements. Other samples were only measured once. The pigment samples are assumed to be rather homogenous and would have in the worst case scenario the same level of contamination as the pyrolysis residues.

### Evaluation of the properties of paint based on recycled pigment material

To evaluate the potential of the pyrolysis ash as a pigment the after-treated and mixed materials from pyrolysis experiments 2 and 3 were incorporated into two formulations with high pigment volume concentration (PVC), see Table 9. PVC is given by the volume of pigments divided by the sum of the volume of pigments and volume of binder. A low PVC paint (less pigment, more binder) is expected to be higher in gloss, more adhesive, less porous and more durable than a high PVC paint. The evaluation and the manufacturing of the paints was made by personnel at Akzo Nobel Decorative Paint laboratory in Slough, United Kingdom. The pyrolysis residue was simplified as a mixture of 45.2 weigh percent  $\text{TiO}_2$  and 54.8 weight percent dolomite (compare this to the real composition of the paint before the pyrolysis, Table 8). The  $\text{TiO}_2$  in each formulation was substituted with the corresponding amount of ash on a volume basis ( $\rho_{\text{TiO}_2} = 4.05 \text{ g/cm}^3$ ;  $\rho_{\text{dolomite}} = 2.85 \text{ g/cm}^3$ ) so the  $\text{TiO}_2$  remained constant while virgin dolomite was added so that the total volume of extenders remained the same. The properties of the paints made on recycled material were compared to the properties of standard paints, which were paints with the same formulation but with virgin pigments and extenders. The experiment is classed as a success if performance between standard and the variants with recycled material matched in all of the key paint properties of opacity, gloss, whiteness and durability. These properties were evaluated on test methods that are adapted from ISO tests, see Table 10.

Table 9 Paint formulations used (expressed as wet volume in 100ml of paint). PVC stands for pigment volume concentration.

Material	High PVC formulation 1 with virgin material	High PVC formulation 1 with pyrolysis ash	High PVC formulation 2 with virgin material	High PVC formulation 2 with pyrolysis ash
Latex binder (50% solids)	5.3	5.3	4.4	4.4
Virgin $\text{TiO}_2$	1.5	0.0	0.8	0.0
$\text{TiO}_2$ /Dolomite (recycled)	0.0	4.3	0.0	2.4
Virgin Dolomite	7.4	4.6	2.1	0.5
Other virgin extenders	18.6	18.6	19.4	19.4
Additives	0.6	0.6	1.0	1.0
Water	66.6	66.6	72.3	72.3

Table 10 Methods used to evaluate paint produced from recycled material.

Test Method	Standard	Reference Number
Opacity(98% Spreading Rate)	ISO 6504-3	[80]
Whiteness	ASTM E313	[81]
Yellowness	ASTM E313	[81]
Gloss (85°)	ISO 2813	[82]
Durability (scrub resistance)	ISO 11998	[83]
Colour-difference (DE2k)	ISO 11664-6	[84]

## Results and discussion

### Leaching of pigments: Prestudy for a hydrometallurgical recycling process

The leaching results are presented in Table 11 and Table 12. The concentrations presented are the minimum and the maximum between the duplicates. The concentration is expressed as the ratio between the titanium in the solid sample and the titanium found in the leachate. It can be seen that less than 1% titanium was leached from the samples.

This was only a pre-study to test the feasibility of a hydrometallurgical recycling route. As the amount of leached titanium was very low a pyro route was prioritized but a hydrometallurgical route cannot be totally discarded. Further leaching studies should be done; especially different acid concentrations and elevated temperatures should be tested. One possibility would be to mix paint waste or residues from a pyrolysis process with ilmenite to simulate the situation where paint waste is used as a feedstock for titanium production. An alternative could also be to leach (or dissolve) as much of the other inorganic components in the waste as possible and leave the rutile pigments in the solid residue. This rutile residue could either be evaluated as a pigment or a feedstock for titanium production.

Table 11 Leaching of titanium with concentrated acids. Concentrations are the minimum and the maximum between the duplicates.

Acid	Minimum % Ti in leachate	Maximum % Ti in leachate
H <sub>2</sub> SO <sub>4</sub>	0.5%	0.7%
HCl	0.8%	0.9%
25vol% HNO <sub>3</sub> + 75vol% HCl	0.8%	0.8%
50vol% HNO <sub>3</sub> + 50vol% H <sub>2</sub> SO <sub>4</sub>	0.8%	0.8%
HNO <sub>3</sub>	0.3%	0.4%

Table 12 Leaching of titanium with perchloric acid. Concentrations are the minimum and the maximum between the duplicates.

Acid	Minimum % Ti in leachate	Maximum % Ti in leachate
HClO <sub>4</sub> 0.01M	0.0%	0.0%
HClO <sub>4</sub> 0.1M	0.4%	0.4%
HClO <sub>4</sub> 0.5M	0.7%	0.7%
HClO <sub>4</sub> 1.0M	0.7%	0.8%
HClO <sub>4</sub> 4.1M	0.7%	0.7%

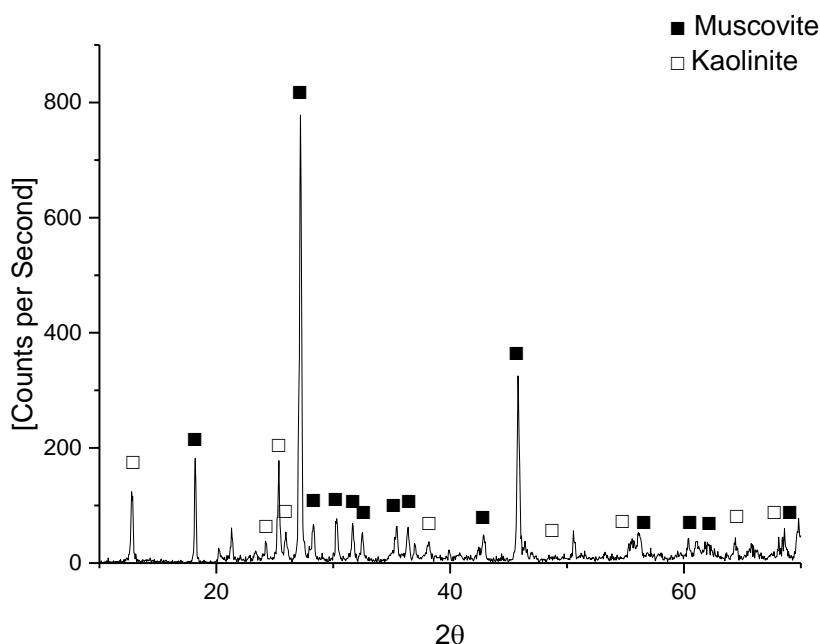


## Characterisation of pigments used in model paint

Note: To separate sample names from mineral names pigment samples will be written with capital letters and in italics.

### Mineralogy by XRD

The X-ray powder diffraction spectrum for the pigment samples provided by Akzo Nobel and the matching spectrum from the database are shown in Figure 7 to



**Figure 11.** An overview of the results is presented in Table 13.

Three of the samples, namely *TiO<sub>2</sub>*, *Kaolin* and *Dolomite*, were identified as pure rutile, kaolinite-1A and dolomite respectively. Only one minor peak at  $2\theta = 17.7^\circ$  in the *Kaolin* spectrum did not match those of kaolinite-1A.

The samples named *Talc* and *Mica* were both shown to contain more than one mineral. The *Talc* contained both talc and clinocllore. There was probably also a small amount of quartz present.

The components in the *Mica* sample were harder to identify. The major part seemed to be muscovite with some kaolinite present but there were peaks at  $2\theta = 12.5^\circ$  and  $25.1^\circ$  that cannot be assigned to muscovite.

Impurities were not surprising as it is not uncommon to use natural minerals as extenders.

Table 13 Overview of the results from sample evaluation with XRD. Samples marked with \* are likely to contain some minor impurities other than those presented.

Name of pigment sample	Compound identified by XRD	Chemical Formula
<b>Dolomite</b>	dolomite	$\text{CaMg}(\text{CO}_3)_2$
<b>Kaolin</b>	kaolinite-1A	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
<b>Talc*</b>	talc clinochlore quartz	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ $(\text{Mg},\text{Al})_6(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_8$ $\text{SiO}_2$
<b>Mica*</b>	kaolinite muscovite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH},\text{F})_2$ or $\text{KAl}_2(\text{SiAl})_2\text{O}_{10}(\text{OH})_2$
<b>TiO<sub>2</sub></b>	rutile	$\text{TiO}_2$

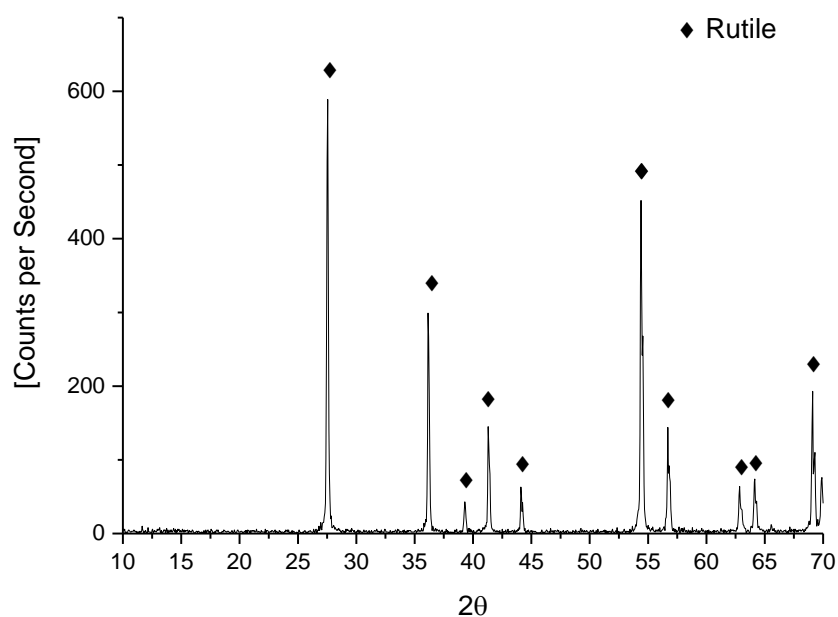


Figure 7 XRD spectrum of Sample  $\text{TiO}_2$ . Intensity in counts per second versus  $2\theta$ . Peak marked with ◆ corresponds to rutile from the database.

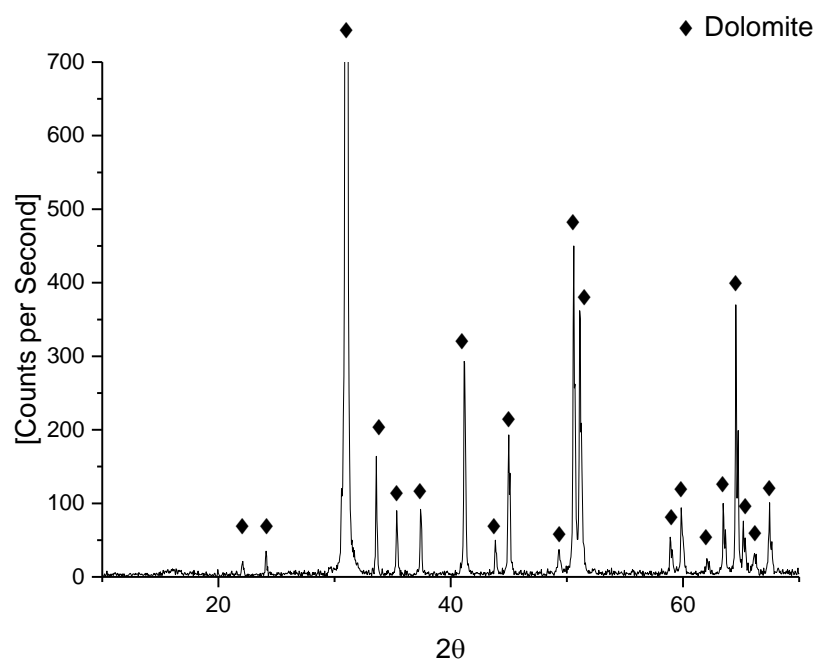


Figure 8 XRD spectrum of Sample *Dolomite*. Intensity in counts per second versus  $2\theta$ . Peak marked with ◆ corresponds to dolomite from the database.

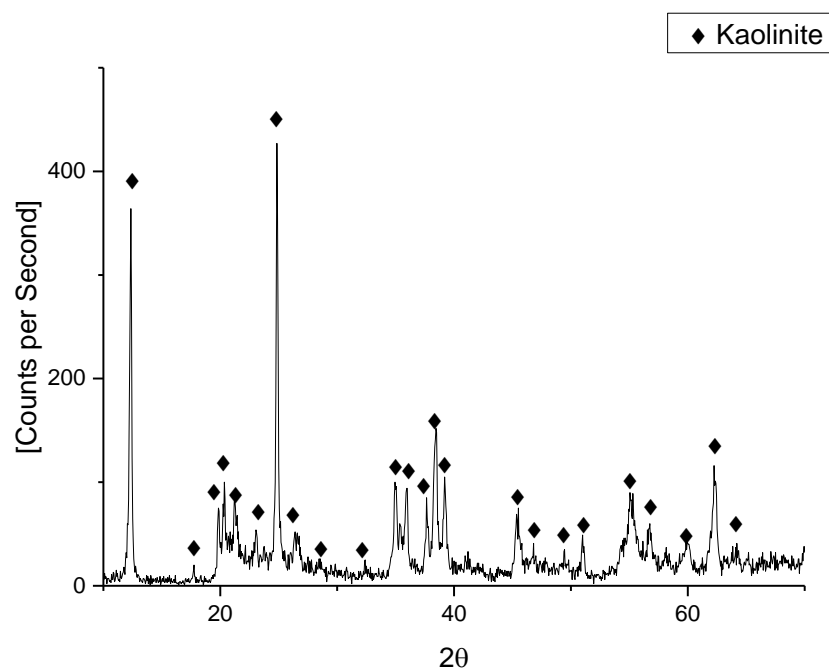


Figure 9 XRD spectrum of Sample *Kaolin*. Intensity in counts per second versus  $2\theta$ . Peak marked with ◆ corresponds to kaolinite from the database.

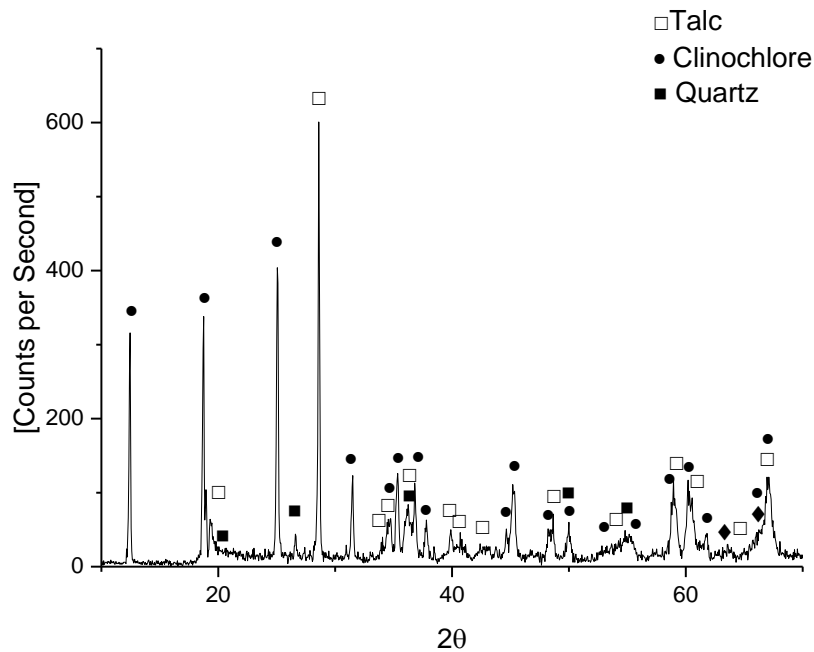


Figure 10 XRD spectrum of Sample *Talc*. Intensity in counts per second versus  $2\theta$ . Peak marked with  $\square$ ,  $\bullet$  and  $\blacksquare$  respectively correspond to talc, clinocllore and quartz from the database.

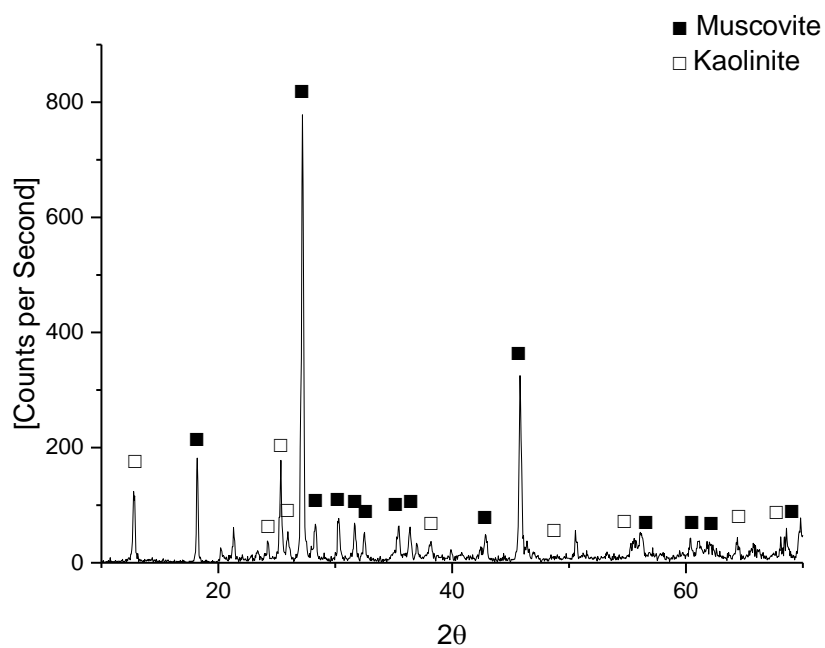
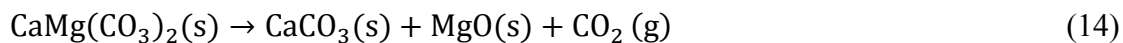


Figure 11 XRD spectrum of Sample *Mica*. Intensity in counts per second versus  $2\theta$ . Peak marked with  $\blacksquare$  and  $\square$  respectively correspond to muscovite and kaolinite from the database.

### Thermal stability of pigments/pigment mix in model paint

The result from the thermal analysis for *Dolomite* can be found in Figure 12 and XRD spectrum of the residues in Figure 13. The *Dolomite* was stable until the temperature reached 700°C. The breakdown occurred through two endothermic reactions. According to the literature dolomite decomposes in two steps into magnesium oxide and calcium oxide [85, 86].



Theoretically a sample consisting of pure dolomite would in the first reaction give a mass loss (due to  $\text{CO}_2$  emission) of 23.9% and the second calcination reaction would bring the total mass loss up to 47.7%. The data from the TGA experiment showed an acceptable agreement with these theoretical mass losses. The XRD spectrum for the residues from the TGA experiments, Figure 13, confirmed that dolomite had been decomposed into MgO (Periclase) and CaO (Lime). As there was no mass loss at temperatures lower than 700 °C there did not seem to be any water adsorbed on the pigment and no organic or inorganic coating present on the pigment that was temperature sensitive.

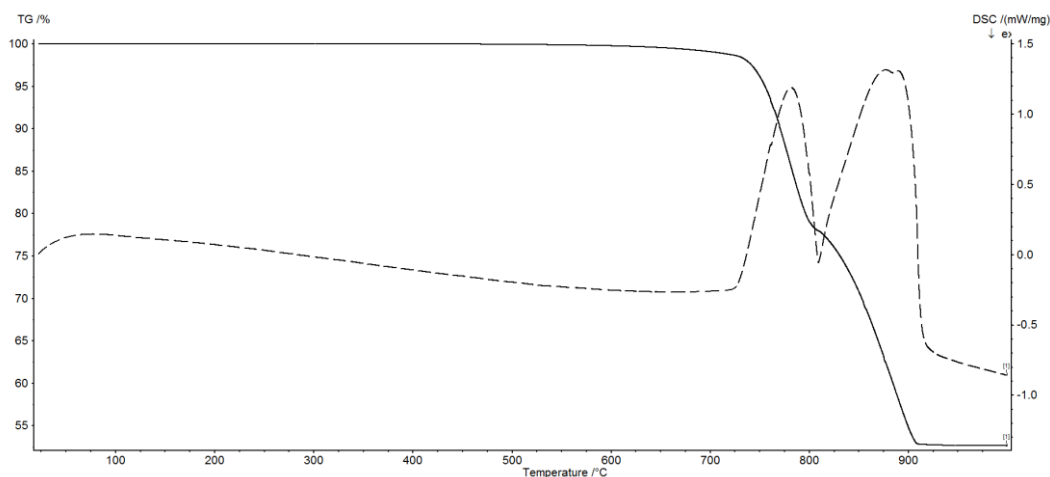


Figure 12 TGA curve (solid line) for sample *Dolomite*. Solid line gives weight loss (in percent) versus temperature (°C). Dashed line is DSC data in which exothermic reactions are given by negative slope.

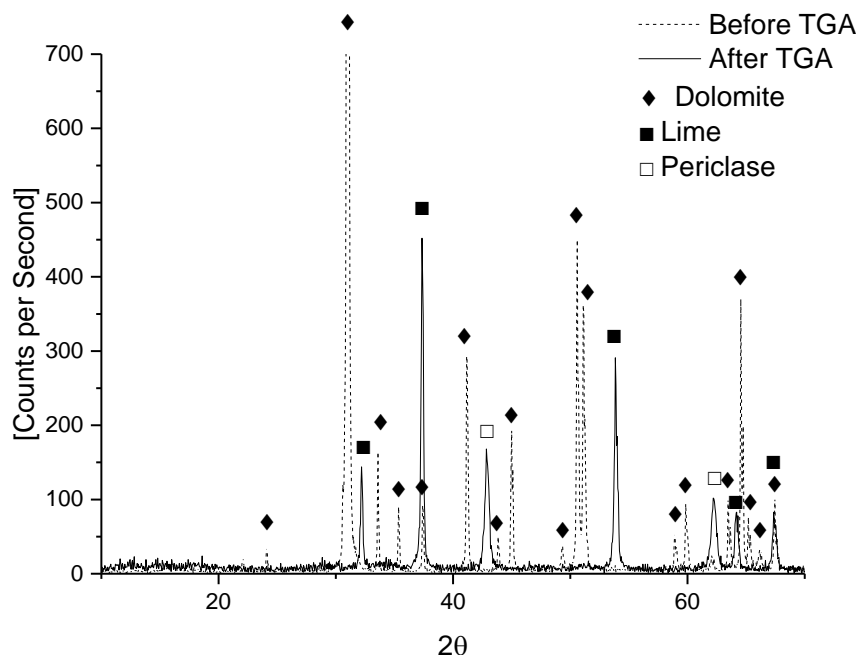


Figure 13 XRD spectrum of the sample named *Dolomite* prior to TGA (dashed line), the residues of sample Dolomite after the TGA experiments (solid line). Peaks for dolomite (◆),lime (CaO) (■) and periclase (MgO) (□) are marked.

According to the literature rutile is stable up to temperatures around 1800°C [20]. The data from the TGA experiments, see Figure 14, showed a total mass loss of roughly 1.5% when the  $TiO_2$  sample was heated up to 1000°C. XRD analysis, see Figure 15, of the  $TiO_2$  sample before and after the TGA experiments verified the inert nature of the rutile. Most of the mass loss occurred in the temperature range 100-500°C. Burfield [87] got very similar results when heating a pigment quality titanium oxide. It is well known that pigments are commonly treated with compounds to improve their dispersion in the paint systems [88]. Thus, it is probable that the mass loss observed in this work is due to the decomposition of such a coating. The mass loss observed at temperatures below 100°C could either be from the decomposition of the coating or loss of surface water. The TGA-data for the  $TiO_2$  pigment sample can be compared to TGA-data for a non-pigment quality of rutile, see Figure 16. This sample did not contain any surface modifications and the inert nature of rutile at temperatures up to 1000°C can clearly be observed as there was no weight loss at temperatures up to 1000°C.

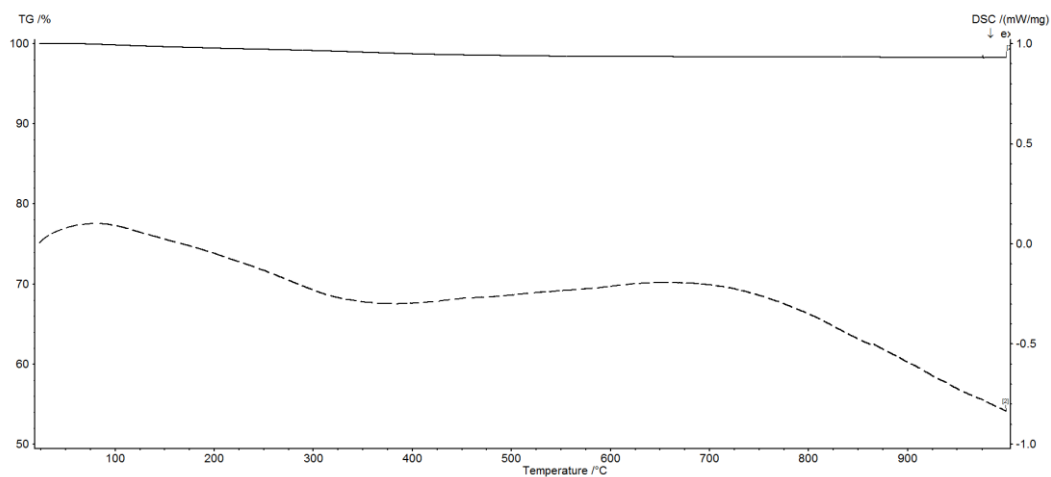


Figure 14 TGA (solid line) results of sample  $TiO_2$ . Solid line gives weight loss (in percent) versus temperature ( $^{\circ}C$ ). Dashed line is DSC data in which exothermic reactions are given by negative slope.

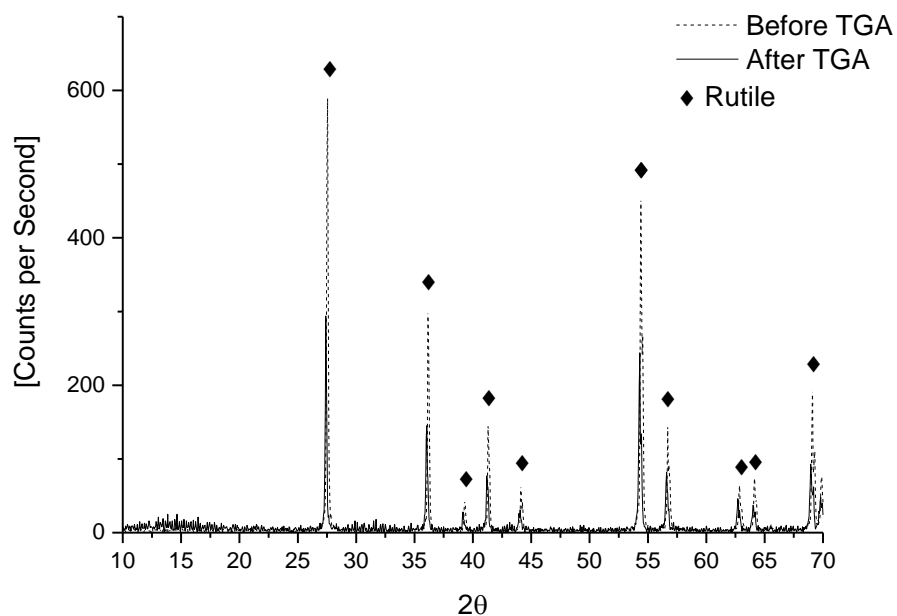


Figure 15 XRD spectrum of the sample named  $TiO_2$  prior to TGA (dashed line), the residues of sample  $TiO_2$  after the TGA experiments (solid line). Peaks for rutile are marked with  $\blacklozenge$ .

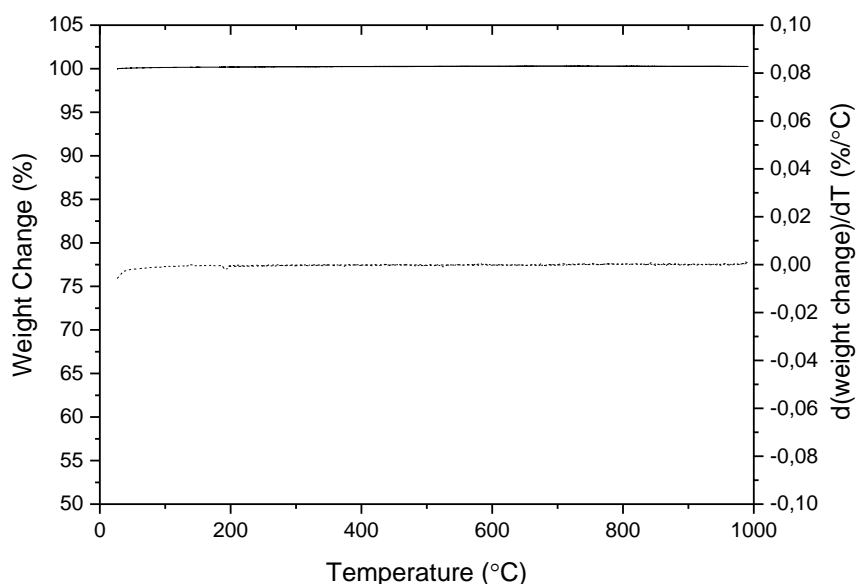
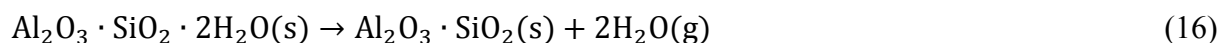


Figure 16 TGA results (solid line) for rutile, non-pigment quality sample. Dashed line is the derivative of weight change with respect to temperature and shows no weight loss during the heating cycle, giving the conclusion that no volatile products were formed.

The sample *Kaolin* was identified as the mineral kaolinite by the XRD spectrum, see previous section. The TGA data, Figure 17 showed a major endothermic peak at 542°C. Comparing this to literature data [89-91] shows that this was probably due to the dehydration of kaolin and the formation of meta-kaolin.



The mass loss rapidly increased above 490°C to a total mass loss of roughly 13%. That fits rather well with the loss of 2 water molecules per kaolin molecule during the dehydration, which would give a mass loss of 14%. At 970°C a strong exothermic reaction started. This was most likely the transformation of metakolin into a cubic spinel phase and amorphous silica [89-91].



The experiment was stopped before the reaction was complete and this explains the highly amorphous structure in the XRD results (see Figure 18). Before the dehydration reaction of kaolin at 542 °C a small mass loss of around 0.7% in the temperature range of 100-500°C was observed. This could be due to vaporisation of surface water or degradation of a surface coating.



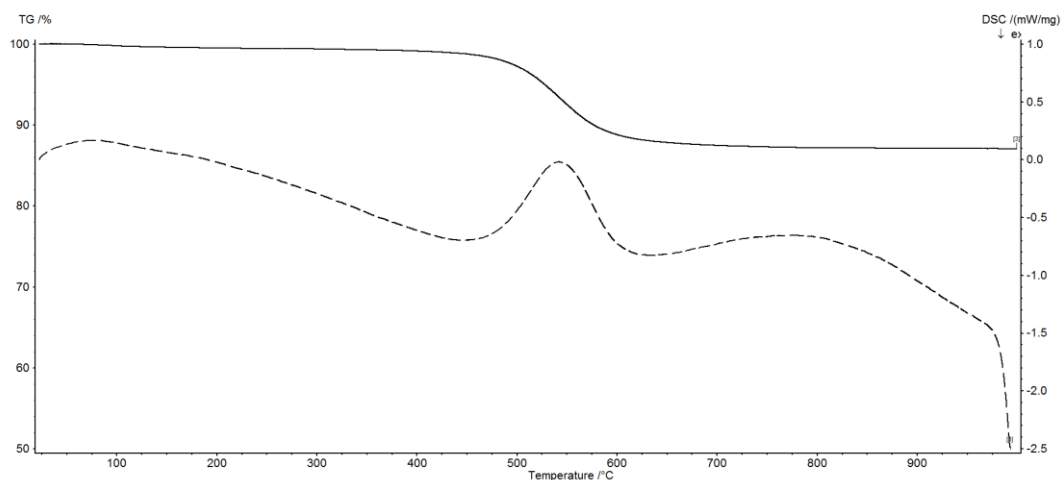


Figure 17 TGA (solid line) results of sample *Kaolin*. Solid line gives weight loss (in percent) versus temperature ( $^{\circ}\text{C}$ ). Dashed line is DSC data in which exothermic reactions are given by negative slope.

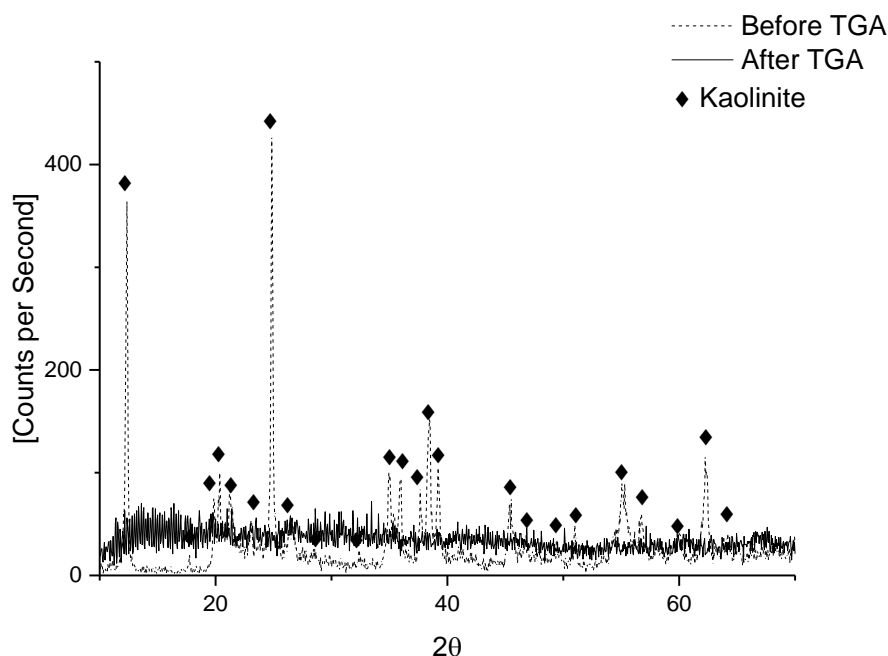
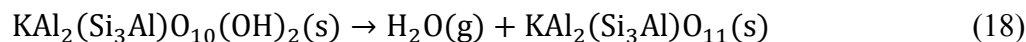


Figure 18 XRD spectrum of the sample named *Kaolin* prior to TGA (dashed line), the residues of sample *Kaolin* after the TGA experiments (solid line). Peaks for kaolinite are marked with ◆.

It is believed that muscovite in the *Mica* dehydroxylates via the following reaction [92, 93]



The dehydroxylation reaction given above gives a theoretical mass loss of 4.5%. This fits well with the final mass loss observed in the TGA experiment (Figure 19). The shape of the TGA curve was similar to the curves found in the literature [92, 93]. At low temperatures small weight losses were probably due to loss in surface water. The large wide peak in the range 475-950 $^{\circ}\text{C}$  was due to dehydroxylation. The *Mica* still had a well ordered crystal structure after the TGA experiments, see Figure 20. There is not a complete agreement of the spectrum

prior to and after the TGA, so small changes in the crystal structure have probably occurred but this was not investigated further.

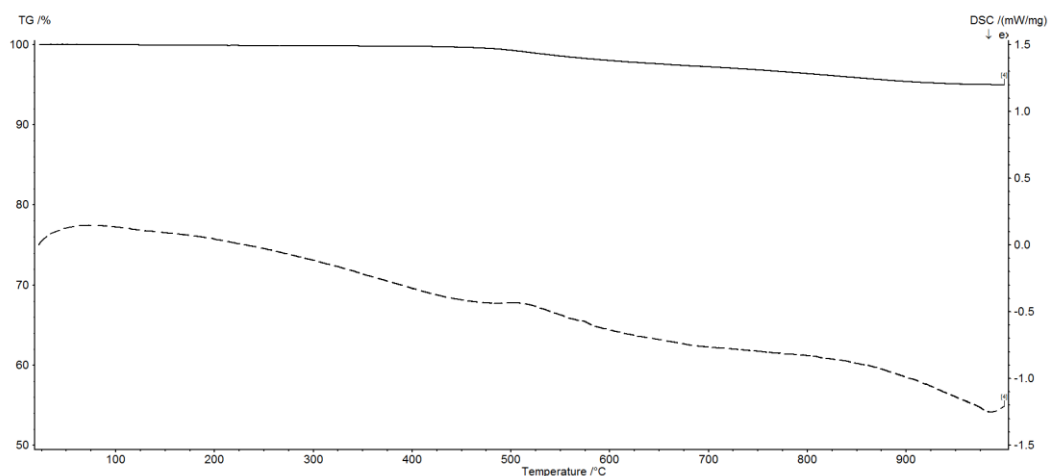


Figure 19 TGA (solid line) results of sample *Mica*. Solid line gives weight loss (in percent) versus temperature (°C). Dashed line is DSC data in which exothermic reactions are given by negative slope.

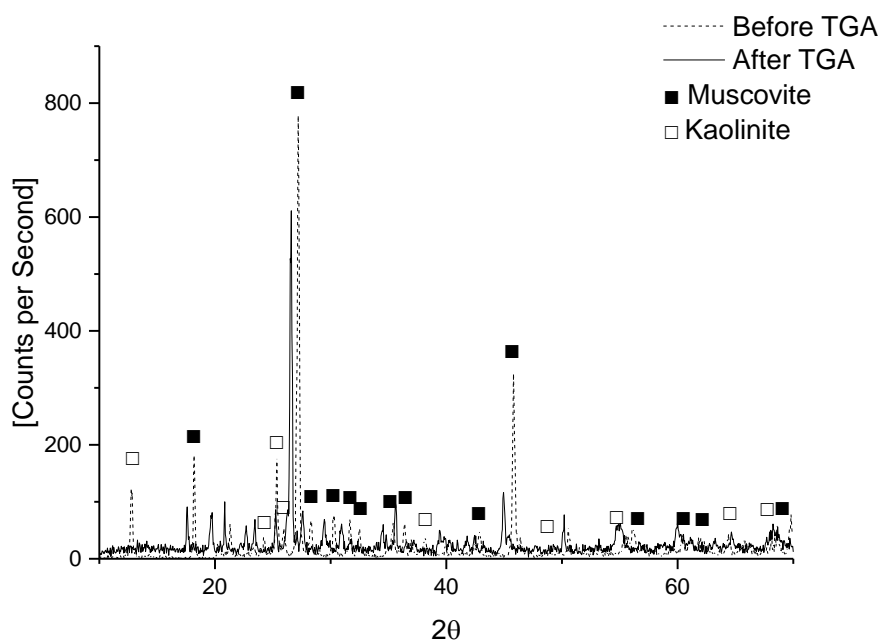
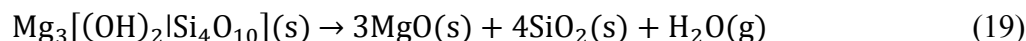


Figure 20 spectrum of the sample named *Mica* prior to TGA (dashed line), the residues of sample *Mica* after the TGA experiments (solid line). Peaks for kaolinite (□) and muscovite (■) are marked.

The sample named *Talc* gave an endothermic peak at 607°C, an endothermic peak at 835°C and an exothermic peak at 870°C, see Figure 21. According to a review article by Wesolowski [94] the first major reaction during the heating of talc is an endothermic reaction that dehydrates the material, followed by various reactions where different crystalline and amorphous magnesium and silica oxides are formed depending on temperature. The dehydration of the talc is described by Wesolowski [94] as:



Both the magnesium oxide and the silica formed are amorphous. The transformation of talc into magnesium oxide and silica would give a theoretical mass loss of 4.8% in the form of water vapour. The total mass loss in the present experiment was closer to 9%. This result, as well as the XRD results described earlier, suggests impurities in the talc sample. The exothermic peak at 870°C could be the formation of crystalline magnesium and silica oxide compounds but this would not give the large change in mass and nothing has been identified in an XRD-analysis of the residues from the TGA, see Figure 22. According to the discussion above is it likely that it is amorphous magnesium oxide and silica.

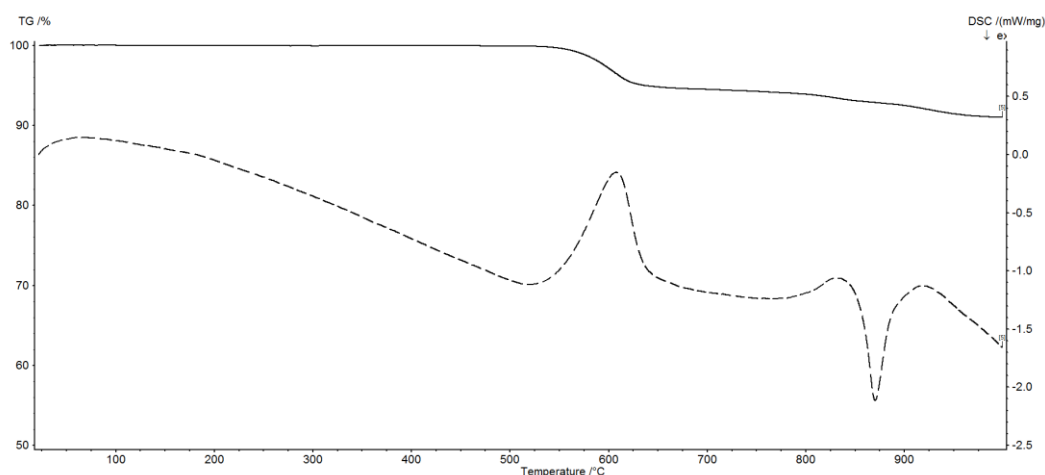


Figure 21 TGA (solid line) results of sample *Talc*. Solid line gives weight loss (in percent) versus temperature (°C). Dashed line is DSC data in which exothermic reactions are given by negative slope.

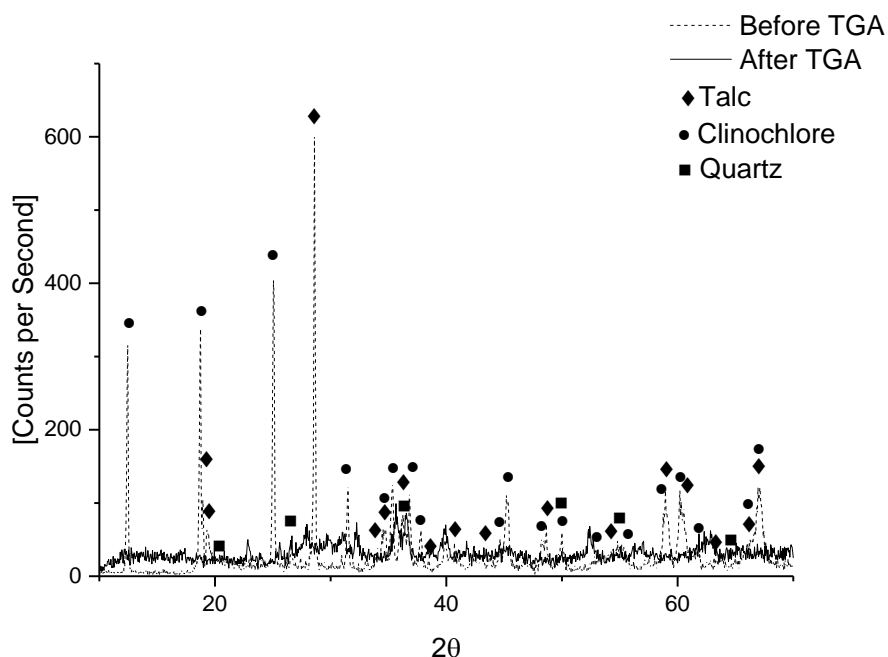


Figure 22 XRD spectrum of the sample named *Talc* prior to TGA (dashed line) and the residues of sample *Talc* after the TGA experiments (solid line). Peaks for talc (♦), clinocllore (•) and quartz (■) are marked.

### ***Conclusion from the evaluation of thermal stability of pigments/pigment mix in model paint***

In conclusion, low temperature (below 100°C) weight losses of the pigments can be due to surface water or possibly organic or inorganic coatings on the pigments. The loss of surface water should not change the crystal structure or influence the optical properties of the pigment. The results presented state that a pyrolysis process at temperatures below 500°C would leave the crystal structure of the inorganic pigments/fillers used in this study unaffected. However, as previously described, surface coating on pigments is a major factor in their performance in a paint matrix. If the coating on a pigment is affected by a heat treatment should it be apparent when the pigment is incorporated into a paint formulation. The TGA/DSC data do not show conclusively if surface coatings are affected. As stated above the weight changes at low temperatures (100°C and below) can be due to transformations of the surface coatings. As the pyrolysis needs to reach temperatures above 400°C (see next section) to break down the binder, the breakdown of the surface coating is unavoidable in this kind of thermal recovery process.

### **Thermal stability of binders**

Note as only weight change was measured is it not possible to say if the binders decompose into non-volatile products. Further DSC analysis would be needed for evaluation of decomposition temperatures.

By viewing the derivate of weight change with respect to temperature it is seen that the vinyl acrylic latex breaks down in two distinct steps at temperatures below 350°C in a nitrogen atmosphere, see Figure 23. The decomposition continued continuously (no distinct steps due to low experimental resolution) at temperatures from 350°C to 500°C until a residue of 5wt% of the original sample remained. The decomposition in synthetic air showed a similar pattern

at temperatures below 350°C, see Figure 25. At temperatures between 350°C and 450°C several reactions are taking place that are impossible to distinguish from each other. Above 450°C the reaction takes place within a sharp temperature interval. The amount of residues seemed to be almost the same as for the experiment done in nitrogen.

The binder based on pure acrylic polymer decomposed in a single step within the temperature range of 310 to 400°C to yield a non-volatile residue of 3wt% of the original sample in nitrogen atmosphere, see Figure 24. When air was present, see Figure 26, the decomposition continued until no non-volatile residues remained. This was probably the oxidation of the char residues formed at temperatures below 400°C.

The thermal decomposition of these binder samples could be studied in greater detail but the aim of this study was mainly to see at which temperature range the binders start to decompose into volatile products. When comparing the thermal decomposition of the binders in nitrogen and in synthetic air the main differences were found at temperatures above the first major decomposition reaction/reactions (350°C and 400°C, respectively). The interaction of air with the organic material and the char residues probably plays a major part above these temperatures but the presence of air does not seem to have any effect on the first decomposition steps. These different decomposition processes are not a focus of this work but can be evaluated in future work, especially if the volatile products of a pyrolysis process or the minimization of carbon containing residues after the pyrolysis process are of interest.

From the results of this study it can be concluded that a thermal process, such as pyrolysis, at 500°C would be sufficient to make most of the binders in a waste paint mixture decompose.

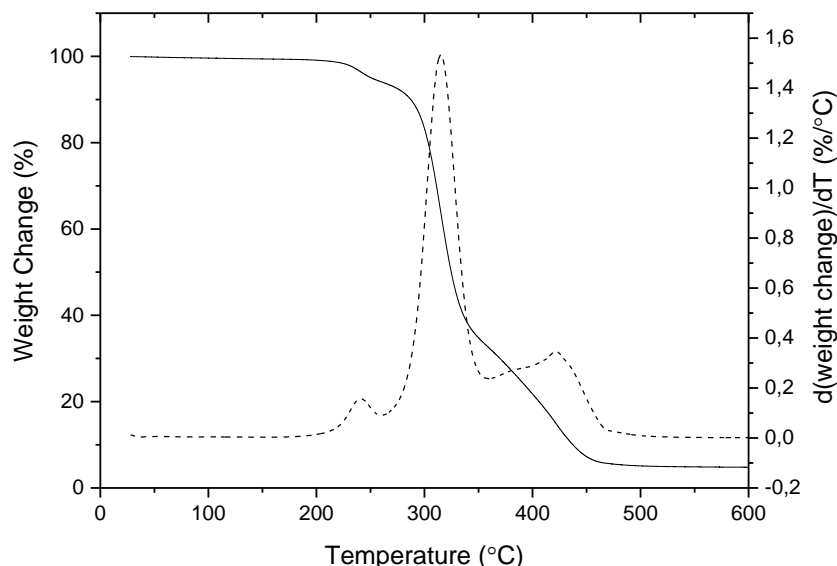


Figure 23 TGA results (weight loss in percent vs. °C) of vinyl acrylic latex in inert atmosphere. Dashed line is the derivative of weight change with respect to temperature.

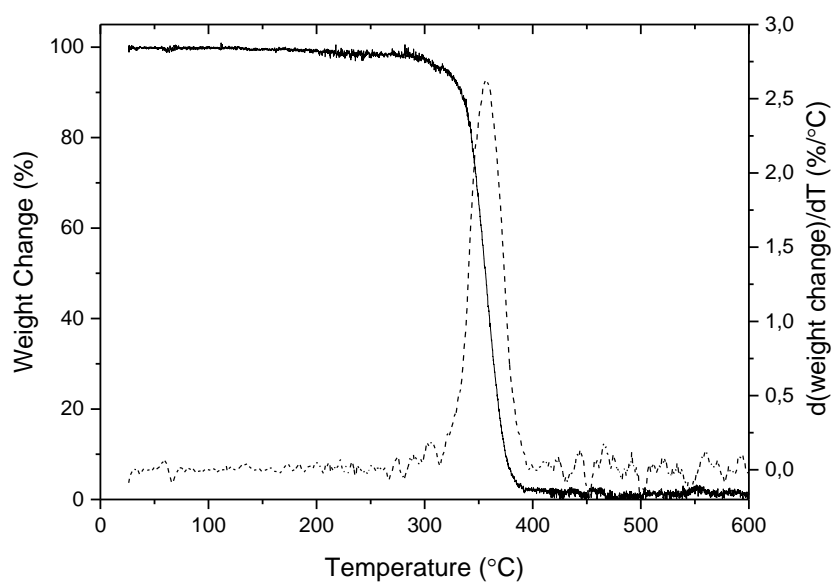


Figure 24 TGA results (weight loss in percent vs. °C) of acrylic latex in inert atmosphere. Dashed line is the derivative of weight change with respect to temperature.

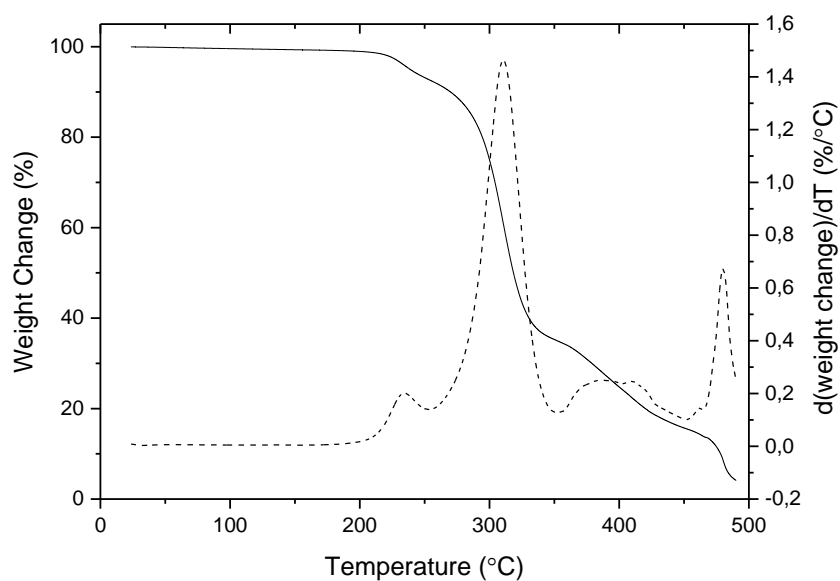


Figure 25 TGA results (weight loss in percent vs. °C) of vinyl acrylic latex in synthetic air. Dashed line is the derivative of weight change with respect to temperature.

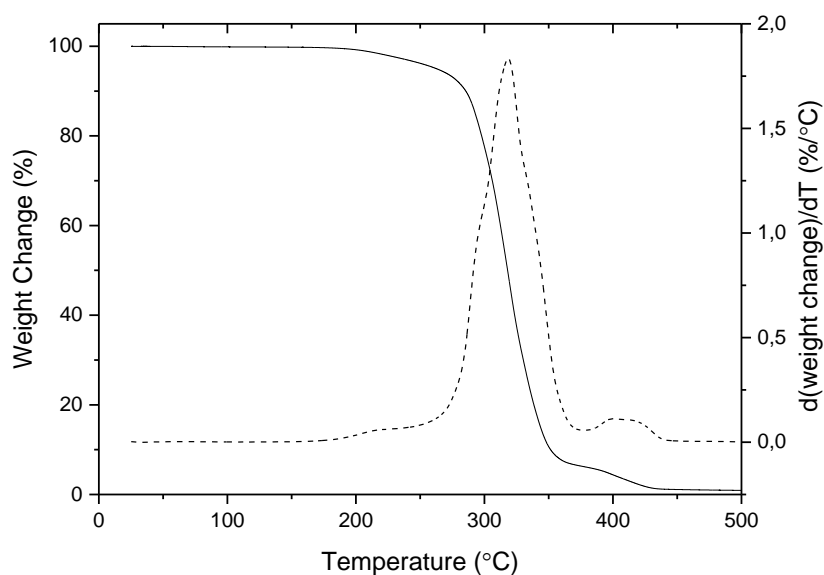


Figure 26 TGA results (weight loss in percent vs. °C) of acrylic latex in synthetic air. Dashed line is the derivative of weight change with respect to temperature.

## Pyrolysis

Data from temperature measurements during the different pyrolysis experiments are shown in Figure 27 to Figure 29 and sample weights before and after the pyrolysis can be found in Table 14. The measured temperatures show a similar behaviour for experiments 1 to 3. First there was a phase of heating of the paint sample (solid line in graphs). In phase two there was a fast increase of the recorded temperature in the gases leaving the pyrolysis vessel (dashed/dotted line in graphs). The temperature reached 100°C and this indicated that the water in the sample started to boil. As the temperature in the gas phase never reached over 100°C water was probably boiled off continuously at the same time as the organic matter in the paint was pyrolysed. In phase three all of the water had been boiled off and the temperature in the gas outlet started to decrease, while the temperature in the sample increased. Here it was assumed that the pyrolysis process was close to complete. When the temperature in the vessel containing the sample reached 500°C the experiments were ended. Gaseous organic matter condenses on the surfaces of the sample vessel. These carbon-containing contaminations capture microwaves and thus the temperature of the vessel increased. This is why the temperature of the vessel wall increased continuously.

In experiment 1 (see Figure 27), the temperature of the pyrolysis chamber increased so rapidly that the magnetrons had to be turned off for the chamber to cool down. After cooling the microwaves were turned on again. Between experiment 1 and 2 the vessel was cleaned of organic residues.

Note that if the weight fractions of the inorganic components (dolomite, kaolin, talc, mica and rutile from Table 8) are summed up together for the wet paint simulation the total is 26.8%.

This value can be compared to the dry fraction residue from the different pyrolysis experiments. Theoretically the dry pyrolysis residue should contain all the inorganic components in the paint and the measured and calculated values show good agreement for experiments 1 and 2. In experiment 3 the dry fraction is larger but is still in the same size range. That means that there was a small amount of organic matter that was not completely pyrolysed in experiment 3. This could be confirmed, as pieces of non-pyrolysed paint could be found in the residues. These pieces of non-pyrolysed paint were removed by hand from the residues before further analysis.

The amount of liquid (the so called oil fraction) produced varied between the experiments. In experiment 1, with the smallest sample size, the vessel temperature was the highest and the smallest amount of condensate was collected. There was also a higher ratio of gaseous phase to condensate produced in experiment 1 than in the other experiments. The main part of the liquid fraction is a transparent aqueous phase that is assumed to be mainly water. The chemical composition of the condensate and gas produced when pyrolysing waste paint will be further investigated in future work.

Experiment 4 (see Figure 30), was carried out using the same paint formulation as in the earlier experiments but the sample material had been dried to a dry content of 65% (compared to 44% for the other experiments) prior to the pyrolysis. The sample still contained some water but the sample was not fluid. It should be noted that it was very hard to raise the temperature in the sample (solid line) over 100°C while the temperature of the pyrolysis chamber (dashed line) rapidly increased to 500°C. The magnetrons had to be turned off for the chamber to cool down but as soon they were turned on again the temperature of the vessel increased rapidly again. This gives the wavelike function of the temperature profiles in Figure 30. As in experiment 1, carbon containing residues were found on the pyrolysis vessel capturing the energy from the microwaves, while the lack of water in the sample made it hard to heat it up. This resulted in an incomplete pyrolysis where big pieces of non-decomposed paint were still present after the pyrolysis. The dry paint sample did not decompose completely even though the experiment was continued for almost 100 minutes. A complete volatilization of the organic components would have resulted in a dry residue of 57wt% (higher than the other experiments due drying before pyrolysis). The solid residue from the experiment was 64wt% (see Table 18). This, together with the non-decomposed paint in the residues, is an indication of the incomplete pyrolysis.

To conclude, it was observed that with the microwave heated pyrolysis equipment used in this work it was difficult to control the pyrolysis process. The main components capturing microwaves in the paint are water and carbon in the form of char. Wet paint is therefore easier to pyrolyse than dry paint. This is probably also due to the fact that the energy can be distributed more evenly in the liquid system.



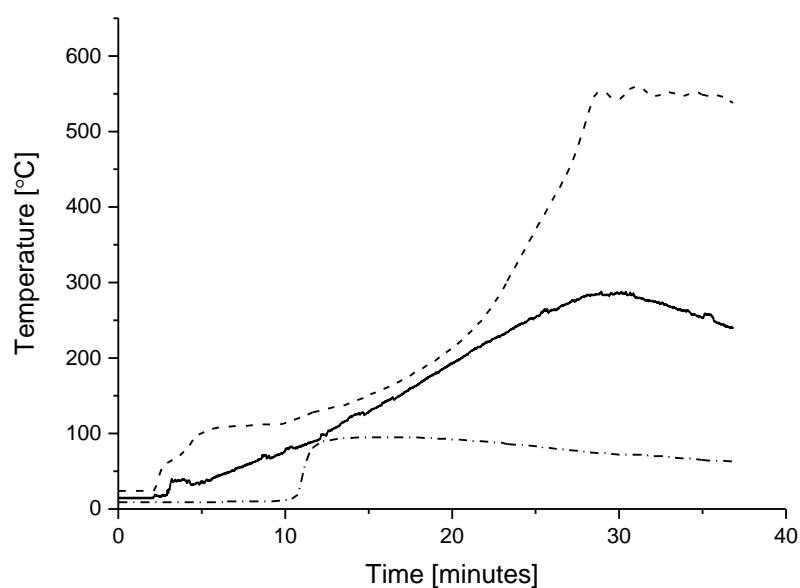


Figure 27 Temperatures over time during pyrolysis experiment 1. The solid line shows the temperature in the sample, the dashed line gives the temperature of the wall of the pyrolysis chamber and the dashed/dotted line gives the temperature of the gases that left the pyrolysis chamber.

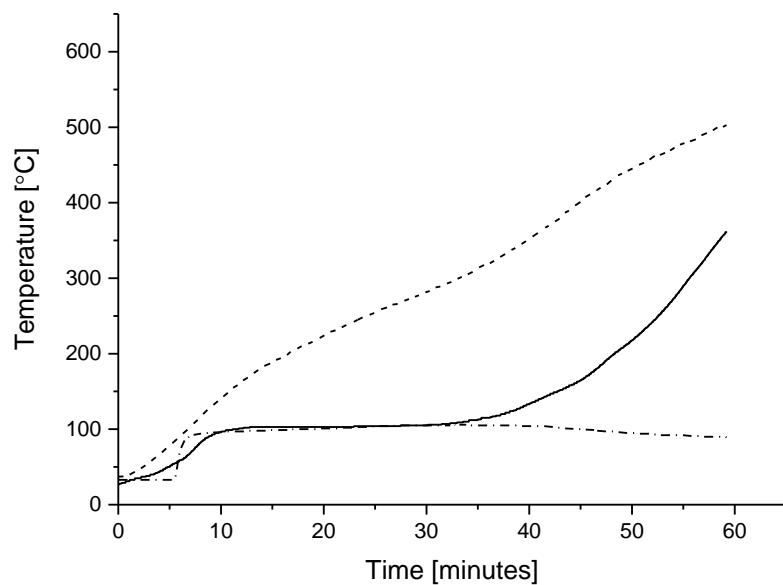


Figure 28 Temperatures over time during pyrolysis experiment 2. The solid line shows the temperature in the sample, the dashed line gives the temperature of the wall of the pyrolysis chamber and the dashed/dotted line gives the temperature of the gases that left the pyrolysis chamber.

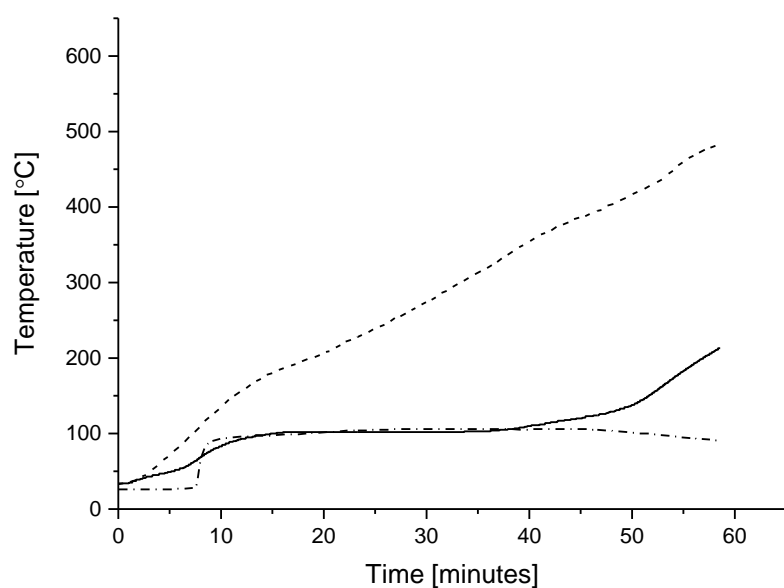


Figure 29 Temperatures over time during pyrolysis experiment 3. The solid line shows the temperature in the sample, the dashed line gives the temperature of the wall of the pyrolysis chamber and the dashed/dotted line gives the temperature of the gases that left the pyrolysis chamber.

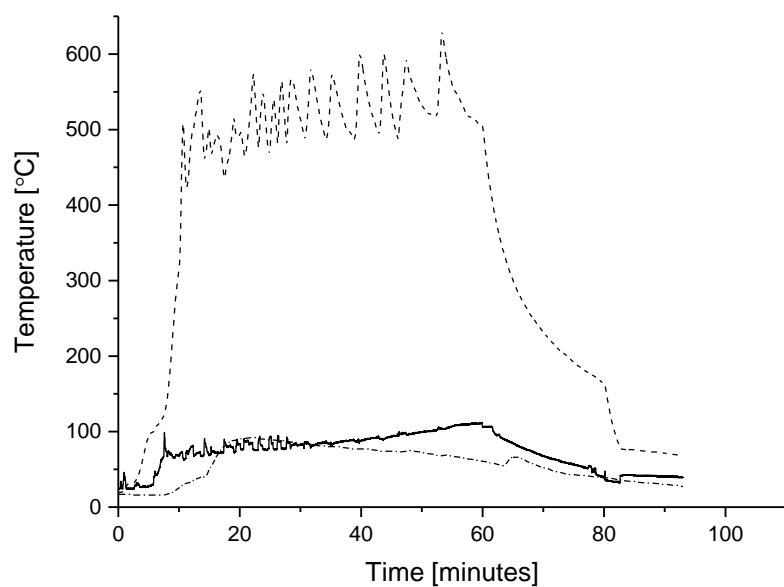


Figure 30 Temperatures over time during pyrolysis experiment 4. The solid line shows the temperature in the sample, the dashed line gives the temperature of the wall of the pyrolysis chamber and the dashed/dotted line gives the temperature of the gases that left the pyrolysis chamber.

Table 14 Weight of samples prior to and after pyrolysis. The weight percent is the ratio of the residue fraction over the sample mass prior to heating.

Sample	Experiment 1		Experiment 2		Experiment 3		Experiment 4	
	Weight (g)	Weight (%)	Weight (g)	Weight (%)	Weight (g)	Weight (%)	Weight (g)	Weight (%)
Sample, prior to heating	241	100%	1450	100%	1624	100%	245	100%
Liquid fraction	112	47%	850	59%	1021	63%	52	21%
Dry fraction	66	27%	398	27%	468	29%	157	64%
Gas fraction (calculated)	63	26%	202	14%	135	8%	37	15%

## After-treatment and characterisation of recovered pigments from pyrolysis experiment 1

Based on a visual evaluation the heat treatment of the solid residue in the presence of oxygen significantly increased the whiteness of the sample, as shown in Figure 31. The heat treatment also resulted in a weight loss of 4% in the sample. The weight change and the change in colour are probably due to the oxidation of char carbon to carbon oxides. However, even if the whiteness is improved by the heat treatment the colour is still quite far from the colour of a mix containing corresponding virgin pigments.



Figure 31 From left to right: virgin rutile pigment, virgin dolomite extender, virgin mica extender, mix of virgin pigments corresponding to the one in the pyrolysis ash, ground pyrolysis ash, heat treated pyrolysis ash.

The XRD spectrum of the ground pyrolysis residue before and after heat treatment can be seen in Figure 32 to Figure 34. If the assumption is made that the solid residue from the pyrolysis process only consists of the inorganic pigments of the pyrolysed paint (see Table 8), rutile and dolomite together make up almost 90wt% of the total residue. This explains their total dominance in the XRD spectrum. The difference in peak height for the reflection for dolomite before and after the oxidation step (Figure 34) is probably due to a preferred orientation of crystals and not to a higher dolomite concentration.

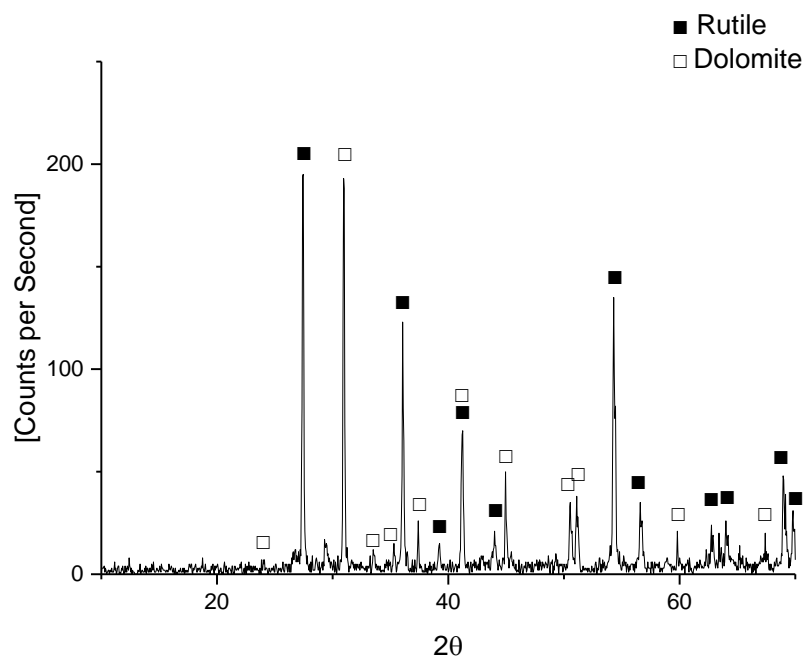


Figure 32 XRD spectrum of ground dry residues from pyrolysis experiment 1. Peaks for Rutile (■) and Dolomite (□) are marked.

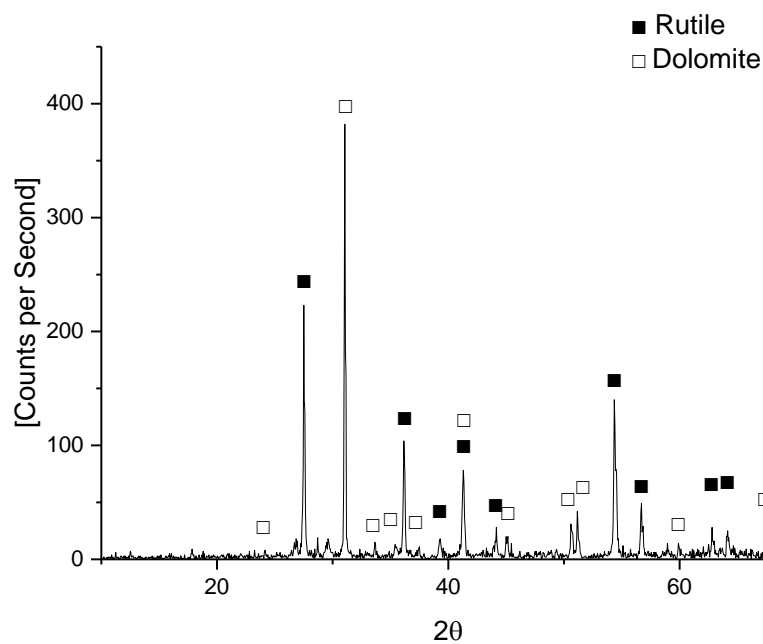


Figure 33 XRD spectrum of dry residues from pyrolysis experiment 1 heated to 400°C in normal atmosphere for roughly 4 h. Peaks for Rutile (■) and Dolomite (□) are marked.

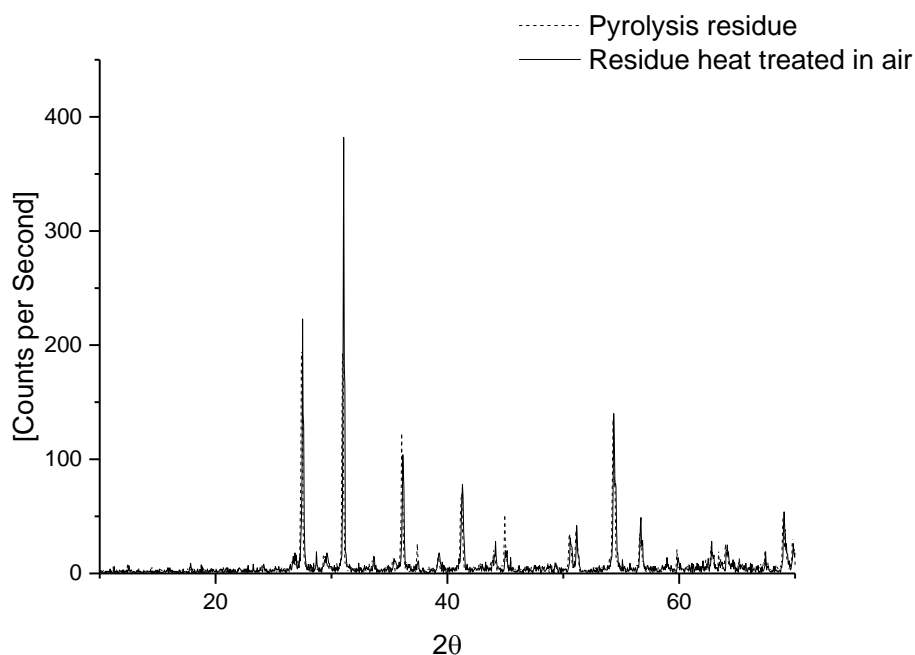


Figure 34 XRD spectrum of dry residues from pyrolysis experiment 1 (dashed line) and spectrum of the same type of sample heated to 400°C in normal atmosphere for roughly 4 h (solid line).

Based on the XRD results the crystal structure of rutile and dolomite seemed to be unaffected by both the pyrolysis process and the after-treatment in normal atmosphere. This is consistent with the previously presented results from the TGA experiments showing that rutile and dolomite are the most temperature durable pigments of those studied here.

Since it was shown that the pigments themselves are unaffected by the heat treatment in air it should be possible to obtain a whiter pigment by oxidizing the residues of carbon-containing compounds in the presence of oxygen or another oxidizing agent. It is plausible that the solid residue from a pyrolysis process using paint waste could be a potential source of pigments.

### **After-treatment and characterisation of recovered pigments from pyrolysis experiments 2 and 3**

The recorded weights of samples of mixed material from pyrolysis experiments 2 and 3 before and after heat treatment in air are shown in Table 15.

In these experiments the weight loss due to the heat treatment was roughly 6-7%. The variations in weight loss between samples are probably caused by non-homogeneity in the pyrolysed material and slight variations in temperature during oxidation.

Table 15 Weights of mixed solid residues from pyrolysis experiment 2 and 3 before and after 450°C for 3 h in air.

<b>Weight before heat treatment [g]</b>	<b>Weight after heat treatment [g]</b>	<b>Remaining material after oxidation</b>
50.31	47.12	93.7%
49.05	45.59	92.9%
52.15	48.74	93.5%
50.40	47.07	93.4%
54.28	50.73	93.5%
64.64	60.51	93.6%
61.71	57.90	93.8%
67.85	63.79	94.0%
62.33	58.49	93.8%
50.36	47.48	94.3%

The XRD spectra for the mixed material from pyrolysis experiments 2 and 3 after heat treatment in air can be seen in Figure 35. It can be seen that the crystal structure of the components, the dolomite and the rutile, were intact. This is similar to what was observed for the oxidised residues from pyrolysis experiment 1. Figure 36 shows the XRD spectrum for the heat treated material and a corresponding pigment mix consisting of virgin pigments in the same composition as that in the pyrolysed paint. Based on the calculations made on the inorganic components in the pyrolysed paint the solid residue consisted of roughly 41% dolomite and 45% rutile. This is reflected in the XRD spectrum, as dolomite and rutile totally dominate. The major parts of the spectrum (dolomite and rutile) were intact but there were peaks at small angles ( $2\theta < 20^\circ$ ) that were not comparable to the published dolomite and rutile spectra. Small angles mean crystal planes with a large distance between them. Most likely this difference in the spectrum was from a collapse of crystal planes in the clay minerals due to heating. Peaks for kaolinite were missing, which means that the kaolinite has decomposed during the recovery process.

The XRD spectra for the oxidized material from pyrolysis experiments 1, 2 and 3 are collected in Figure 37. The placements of the peaks are at the same angles for all spectrums. This suggests that the inorganic residues from the material in the three pyrolysis experiments are very similar in composition. The intensity of the peaks was somewhat different but this was probably due to sample preparation and not in real differences between the samples.

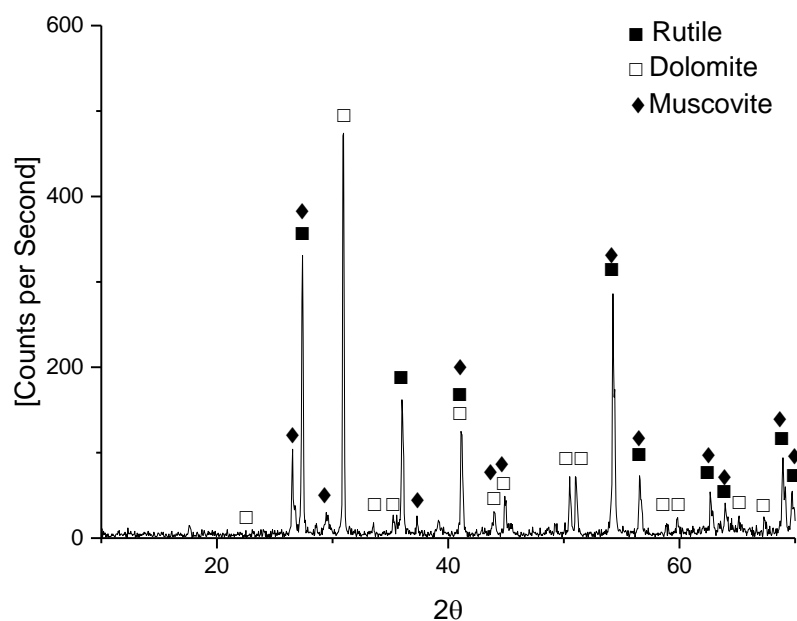


Figure 35 XRD spectrum of mixed solid residues from pyrolysis experiment 2 and 3 after 450°C 3 h in normal atmosphere. Peaks for muscovite (◆), dolomite (□) and rutile (■) are marked.

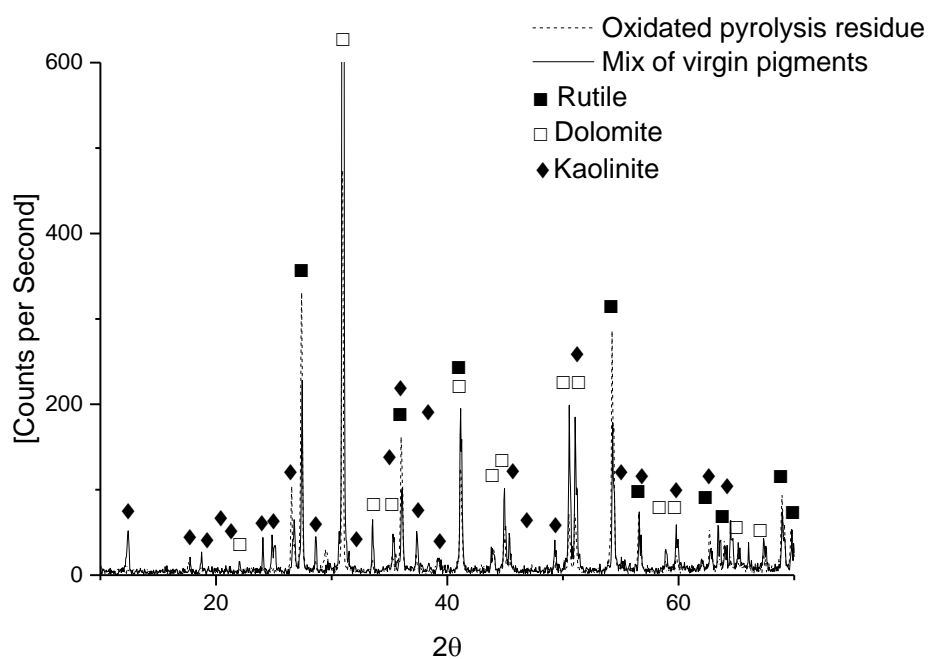


Figure 36 XRD spectrum of mixed solid residues from pyrolysis experiment 2 and 3 before and after 450°C 3 h in normal atmosphere (dashed line) and a mix of corresponding virgin pigments (solid line). Peaks for kaolinite (◆), dolomite (□) and rutile (■) are marked.

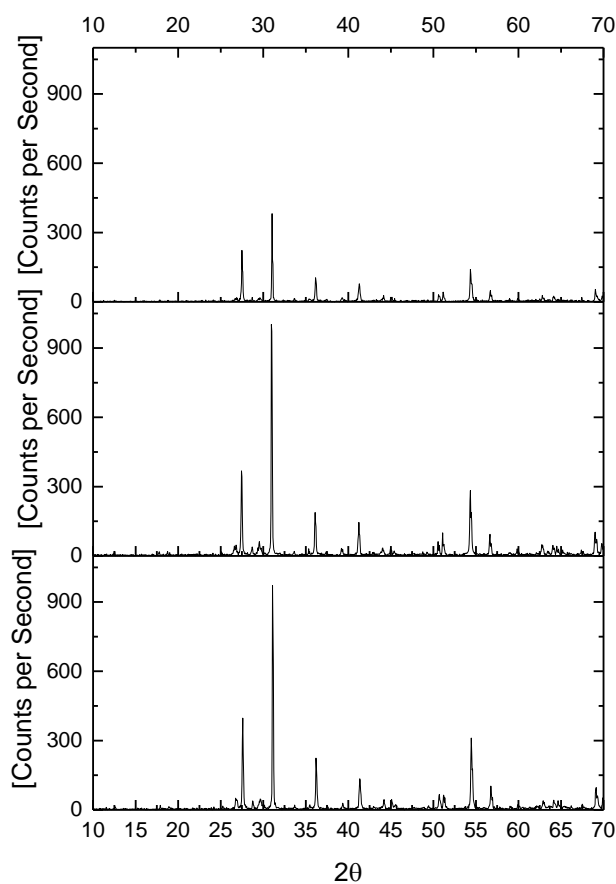


Figure 37 XRD of the heat treated residues from pyrolysis experiment 1 (topmost), pyrolysis experiment 2 (middle) and pyrolysis experiment 3 (bottom)

The results from the BET measurements can be found in Table 16 and Table 17. The BET surface area is lower for the pyrolysis residues than that for the original mix of pigments. This suggests that even though the XRD shows that the crystal structures are intact the pigments are affected by the pyrolysis process. A sintering effect would have given a reduced surface area, but without a particle size measurement or a SEM view it is hard to say what happened. BET measurements on individual pigments suggest only the rutile pigment was affected by heat treatment, as can be seen in

Table 13. No significant changes in surface area were observed for the other pigments. Also the non-pigment quality of rutile was unaffected by the heat treatment. It is known that most titanium dioxide pigments are surface coated. Most probably the surface coating of the  $\text{TiO}_2$  pigment has been destroyed. If this is true this would have an effect on the properties paint films in which this pigment is incorporated.



Table 16 Results from BET measurements made in triplicate on pigments and mixed pyrolysis residues from experiment 2 and 3 before and after heat treatment in air at 450°C for 3 hours, as well as a mix of virgin pigments corresponding to the pigments in the pyrolysed paint.

Sample	BET [m <sup>2</sup> /g] Average Std.Dev	
Pyrolysis Residue	6.33	0.11
Heat treated Residue	6.53	0.27
Pigment mix	9.71	0.31

Table 17 Results from BET measurements on virgin pigments before and after heat treatment in air at 450°C for 3 hours

Pigment sample	Mass loss due to heat treatment	BET [m <sup>2</sup> /g] Heat treatment	
		Before	After
<i>Dolomite</i>	0.3%	0.8	0.7
<i>Kaolin</i>	9.7%	14.5	14.5
<i>Talc</i>	0.2%	4.9	4.3
<i>Mica</i>	1.6%	3.5	3.0
<i>TiO<sub>2</sub> (rutile)</i>	1.3%	17.2	12.2
Non-pigment rutile	0.0%	2.6	2.7

## Paint properties of paint based on recycled material

All methods used for the evaluation of the paints based on virgin and recycled material and the corresponding results are given in Table 18.

Table 18 Results of paint parameters for paint based on virgin and recycled material

	Method	High PVC formulation 1	High PVC formulation 1	High PVC formulation 2	High PVC formulation 2
		with virgin material	with pyrolysis ash	with virgin material	with pyrolysis ash
Opacity(98% Spreading Rate)	ISO 6504-3	8.3	11.0	5.6	7.6
Whiteness	ASTM E313	83.15	78.11	80.90	74.75
Yellowness	ASTM E313	2.88	3.34	3.50	3.80
Gloss (85°)	ISO 2813	14.9	12.3	10.4	9.6
Durability (scrub resistance)	ISO 11998	0.9	1.3	8.9	11.1
Colour-difference (DE2k)	ISO 11664-6	N/A	1.1	N/A	1.6

Table 19 Simplified overview of expected whiteness and yellowness of different formulation types. Standard data provided by Akzo Nobel Decorative Paints.

Formulation Type	TiO2 content	Expected Whiteness Range	Expected Yellowness Range
<b>Silk/Softsheen/Premium Matt</b>	High	91 – 86	1.0 – 2.0
<b>Mid Tier Matt</b>	Moderate	86 – 82	2.0 – 3.0
<b>Low Tier Matt</b>	Low	82 – 78	3.0 – 4.0

Before the impact on performance based on the inclusion of this new raw material can be discussed, some experimental observations need to be considered. Firstly, the recycled material was not fully dispersed into the paint system, resulting in film defects (see Figure 38). This effect was seen even when increased dispersant levels were added to the formulation. Secondly, the change in colour from the raw material causes false positives in some of the paint testing. The grey colour impacts the opacity results, as the calculation is based on coverage over a white and black area, which can be impacted by paint colour.

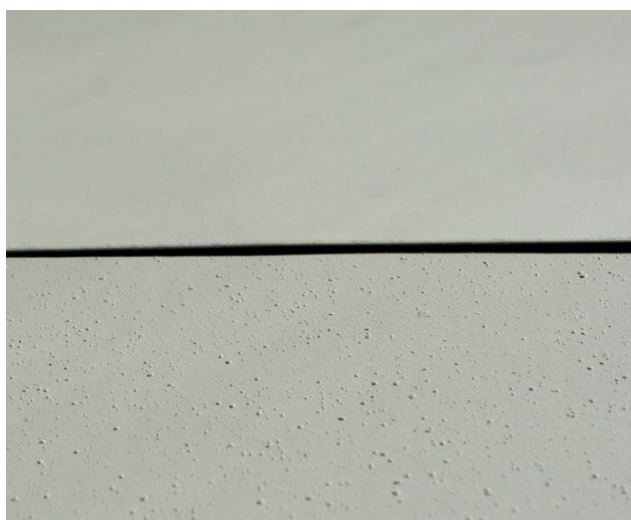


Figure 38 Picture of paint films made with virgin pigments (top) and recycled pigments (bottom). Real length of paint sample shown is 10cm.

To help describe the paint results the roughly expected measuring values for different paint qualities can be found in Table 19. Effectively, the substitution of the virgin pigments with the recycled materials has impacted the product performance by changing it from a Mid Tier Matt performance to a Low Tier Matt performance in terms of whiteness and yellowness. The point of interest that was highlighted with these results was that the effect on whiteness is more significant than the effect seen on the yellowness. Although Whiteness and Yellowness are generally secondary paint properties, an indicative change in acceptable results for these in absolute terms would be a Whiteness decrease of 1 to 1.5 units and a Yellowness increase of 0.3-0.5 units.

Based on the two issues discussed above, the true extent of performance impact of the recycled material is difficult to fully analyse. The results of the key properties can be expressed as:

- Opacity – a false positive was observed based on the grey hue of the paint influencing the spreading rate calculations (this method includes absorption and scatter contributions so the colour will have an impact on the observations.)
- Gloss - equivalent for both formulations (the film defects problem is hidden by matt formulations)
- Whiteness and yellowness index – significant drop in paint whiteness (large impact by grey nature of the recycled  $\text{TiO}_2$ ) but equivalent yellowness
- Durability – slightly reduced performance (based on increased dispersant levels)

From these experimental results, the recycled pigments cannot be used as a direct replacement when formulating. However, before the material can be approved or rejected for use in formulating the issues of poor dispersion and colour change need to be resolved to enable an investigation of the impact of the recycled material when incorporated into a paint film. To ensure the raw material has been properly used, raw material dispersant demands need to be investigated to ensure the correct level of dispersant is used when formulating with the recycled material. The level of dispersant and the type of dispersant are dependent on the surface chemistry of the recycled pigment. Thus, it is necessary to further study how the recycling process affects the surface of the pigment. This can be done with SEM, dispersant demand tests and titration of acid/base surface groups.

When these factors have been investigated, new pyrolysis and oxidation experiments should be designed to optimise the recovery of pigments. The possibility of a surface treatment to be added to the recovered pigments to improve their dispersibility should also be investigated.

## Conclusion

Titanium dioxide is an essential raw material for the paint industry. Due to increased prices and large environmental impact in the production of virgin material, the paint industry is looking for alternative sources for this vital white pigment. The objective of the work in this thesis was to investigate if the residues from pyrolysis of paint containing several types of inorganic pigments could be used as a pigment replacement in new paint.

A thermogravimetric study gave the temperatures that would break down the binders in the paint waste into volatile products but still leave the crystal structure of the pigment intact. The binders decomposed at temperatures below 500°C while all the pigments showed very little to no weight loss at temperatures up to 500°C. It was concluded that the pyrolysis process would operate at a maximum temperature of 500°C. The pyrolysis process was based on microwave heating. Pyrolysis experiments were done on both wet and dry paint. Wet paint was pyrolysed successfully, leaving an amount of inorganic residues comparable to the amount of inorganic pigments in the pyrolysed paint. The pyrolysis of dry paint was incomplete as the material was unable to capture the microwave energy.

The inorganic residues from the pyrolysed wet paint were heat treated in air at 450°C for 3 hours to improve the whiteness. XRD analysis of the pyrolysis residues before and after the heat treatment in air confirmed the crystal structures of the pigments were left intact. However, BET measurements showed that the recycling process had reduced the surface area of the rutile pigment. It was assumed that this reduction in surface area was due to destruction of the surface coating on the pigment.

The recycled material was used in two types of paint formulations as a pigment replacement and the properties of the paints were evaluated and compared to those of a standard paint formulation containing only virgin pigments. The results in opacity and gloss were comparable to the standard, but a decrease in whiteness and poor dispersibility made the quality of the paint based on recycled material inferior to the paint based on virgin material. The reduction of whiteness was assumed to be due to carbon-containing residues from the pyrolysis process and the poor dispersibility was assumed to be due to the destruction of the surface coating of the pigment. More research is needed as the pyrolysis residues could not be used to replace virgin pigment without reducing the quality of the final product.

The result of an additional leaching study of rutile in strong acids is also presented. The purpose of this study was to investigate if rutile in paint waste could be leached and recovered via a hydrometallurgical recovery route. The acids used in this study were concentrated H<sub>2</sub>SO<sub>4</sub>, HCl and HNO<sub>3</sub>, a mixture of concentrated HNO<sub>3</sub> and HCl, a mixture of concentrated HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> at concentrations of 0.01 M, 0.1 M, 0.5 M 1.0 M and 4.1 M. Less than 1% of the titanium was leached and a hydrometallurgical recovery route was therefore not seen as a favourable recovery route when compared to a pyroprocessing route.

## Future Work

This work can act as a foundation for pigment recovery from paint waste, but several different questions need to be addressed. The pyrolysis and the after-treatment need to be optimized to keep the carbon containing residues to a minimum, as these affect the final colour of the product. The effect of temperature, time and atmosphere requires more evaluation. Maybe gasification in the presence of air could be a viable option. Investigations using a paint formulation based solely on titanium dioxide as an inorganic component could make it easier to evaluate the properties of a recycled  $\text{TiO}_2$  pigment. The formulation in this work contained different inorganic pigments that complicated the analysis work. At the same time more complicated formulations must be tested to more appropriately simulate a real paint waste stream. This could include different kinds of inorganic and organic pigments, different binders and maybe even substrates such as wood or plastic containers containing their own mix of pigments and extenders. A way to increase the value of the residue from a thermal process would be to try to separate titanium dioxide from the less valuable extender pigments. This could be achieved through particle size or density separation, or froth flotation.

The quality of the recycled material must also be studied further. The BET measurements need to be combined with particle size measurements and SEM. To understand the poor dispersibility of the pigment the surface chemistry of the recycled pigment must be investigated. This can be done with potentiometric titrations and evaluation of the zeta-potential of the pigment. Fourier Transform InfraRed (FT-IR) spectroscopy can also be used to study the chemical groups on the surfaces of pigment particles.

This study was done at relatively low temperatures to keep the pigments intact. A high temperature process might give reactions that create titanium species which are easier to leach in a hydrometallurgical process.

If the pigment quality is deemed too low the pyrolysis ash could potentially be used as a feedstock for today's titanium dioxide production. A residue pure enough might even go into a chloride route and the paint waste may finally end up as precious titanium metal.

This has been only a pre-study to test the feasibility of a hydrometallurgical recycling route. Based on these results a pyro route was prioritized, but a hydro hydrometallurgical route cannot be totally discarded. Further leaching studies should be tested, especially using different acid concentrations and elevated temperatures. One possibility would be to mix paint waste or residues from a pyrolysis process with ilmenite to simulate the situation where paint waste is used as a feedstock for titanium production. An alternative could also be to leach (or dissolve) as much of the other inorganic components in the waste as possible and leave the rutile pigments in the solid residue. This rutile residue could either be evaluated as a pigment or a feedstock for titanium production.

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# Paper I



# Recovery of titanium dioxide and other pigments from waste paint by pyrolysis

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## Abstract

In this work a model paint containing several types of inorganic pigments was pyrolysed in a microwave heated unit. The goal of the pyrolysis process was to recover and recycle the inorganic components in the paint most importantly titanium dioxide (TiO<sub>2</sub>). The solid residue remaining after pyrolysis was further heat treated in air to produce a TiO<sub>2</sub> containing product.

The recovered TiO<sub>2</sub> containing product was used in two types of paint formulation as a replacement for virgin TiO<sub>2</sub>. The properties of the paints containing recycled TiO<sub>2</sub> pigment were evaluated and compared to standard paint formulations containing only virgin TiO<sub>2</sub> pigments. A drop in paint whiteness was observed but the opacity, gloss and durability was nearly equivalent to the standard paint. Another consequence of using recycled pigments was inferior dispersibility of the recycled mix of TiO<sub>2</sub> pigments and extenders in the paint giving the painted surface an undesirable rough texture. The recycled material showed promise as a pigment/extender but further studies are needed to optimize the recycled product to meet whiteness and dispersions requirements for incorporation paint formulations on a industrial scale.

## Keywords

Titanium dioxide recycling, TiO<sub>2</sub>, paint waste recycling, pigment, extender, pyrolysis

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## 1. Introduction

The U.S. Geological Survey estimated that in year 2011 the total world mining production of ilmenite and rutile ore, the two major mined titanium minerals, was 6.7 million metric tonnes [1]. 95% of the mined titanium minerals were used in the production of titanium dioxide [2]. About 90% of the TiO<sub>2</sub> is used as a pigment and the majority of this in paint and coatings. Due to the heavy use of titanium dioxide in architectural coatings the activity in the construction industry has an especially strong effect on titanium dioxide demand [3]. While several non-pigment uses exist for titanium dioxide, the most important use is as a white pigment in a wide range of products, for example, paint, plastics and paper.

In relation to paint the most important qualities of a white pigment is its ability to give the paint white colour and have high opacity to cover the substrate on which it is applied. TiO<sub>2</sub> appears white due to its ability to scatter visible light. TiO<sub>2</sub> in the rutile form is however not perfectly white since it absorbs some of the light in the 400-500nm region, thus giving more cream-toned whites [4]. High whiteness has a direct correlation to chemical purity, especially the absence of transition metals and compounds thereof. To optimize the TiO<sub>2</sub> performance as a pigment it is washed, filtered and milled to the right particle distribution size. Typically TiO<sub>2</sub> pigment is given a surface treatment to optimize desirable qualities such as dispersibility, opacity and

gloss [5].

Mineral pigments or extender pigments have traditionally been used to dilute a more expensive product without compromising on the desired qualities. Nowadays almost all extenders can be seen as functional fillers with their own purpose and function in a coating formulation. The carbonates are probably the most used extenders based on weight consumed but they can be replaced with another extender more abundant in the area. This gives large variations in coating formulations depending on which extenders are available at a close distance. Common complements/replacements for carbonates are kaolin (kaolinite) and talc [4].

Due to the high demand of  $\text{TiO}_2$  the increased price level and the high environmental impact of producing virgin  $\text{TiO}_2$  new innovative ways of titanium dioxide production are needed. The European Union (EU) has recognized the environmental impacts of titanium dioxide production and has thus put restrictions on the amount of titanium dioxide that is allowed to be used in paint formulations in order to qualify for the voluntary EU Ecolabel [6]. A possible new source for titanium dioxide can be recovery, from different waste materials such as paint waste. Today, processes for recovery of titanium dioxide are non-existent. Recovery of  $\text{TiO}_2$  from paint waste is of interest due to its relatively high  $\text{TiO}_2$  content and its abundance as a reasonably homogeneous waste stream. Not only could a recycling process give paint manufactures a new source for pigment, it also gives the industry a way of handling their production waste and leftover paint products.

From a larger perspective the reuse of old paint, either directly or as a component in new batches of paint is a straight forward approach and initiatives in this direction have been made [7, 8]. A company in the United Kingdom left over paint has been collected, processed and incorporated in new paint[7]. Another initiative is the Community Repaint organisation in UK that is collecting and distributing usable waste paint to people and organisations needing paint [8]. However, this option is not always applicable due to dry non dispersible paint lumps, incompatible paint components, microbiological contamination and the changing chemical and biocide regulations that would make the new paint batch unusable from a legal perspective. Instead, the main existing waste management processes for paint have been designed with the aim to reduce the volumes of waste. In Sweden paint cans and paint waste together are a major part of the hazardous waste stream from households and industry. The packaging is normally sorted separately while the paint residues are incinerated and the resulting ashes are landfilled [9].

Gasification or pyrolysis of paint waste or used plastic paint containers as a method for recycling of paint components and the value of these components has been described in literature [10-14]. In the described methods the organic components in the paint were viewed as the valuable part to be used for energy production. No work on the recovery of the inorganic parts ( $\text{TiO}_2$  containing pigments) has been found in the literature thus far.

In the present work, inorganic pigments are considered to be the most valuable part of the waste paint. The aim of this work was to investigate if the inorganic,  $\text{TiO}_2$  containing residues (pigments) resulting from pyrolysis of waste paint can be used as a replacement or partial replacement for virgin pigment and fillers in paint formulations. The gas and the oil produced from the pyrolysis fraction could potentially be used as an energy source or a raw material for synthesis of chemicals but at the moment that is out of the scope for this work.

## 2. Material and methods

### 2.1 White model paint

TiO<sub>2</sub> in the rutile form along with some common extender pigments were procured from commercially available sources. The extenders chosen for this study were dolomite, kaolin, talc and mica. Unless otherwise stated, the pigments were used as delivered from Akzo Nobel Decorative Paint.

A model paint containing all the pigments/extenders was produced according to the formulation shown in Table 1. The equipment for mixing and paint preparation in the laboratory of Akzo Decorative Paints in Slough, UK was used. In addition, a mixed pigment sample corresponding to the pigment composition in the model paint was prepared by mixing dry pigments together, see Table 1 for composition. Two types of binders were used acquired, a vinyl acrylic latex copolymer with acrylic latex and a pure acrylic latex binder. These two binders are assumed to correspond to the major types of binders which can be found in paint waste. Both contain 52 weight percent polymer and 48 weight percent water. A non-pigment quality of rutile (particle size <5 µm, purity ≥99.9%) to be used for comparison with pigment quality rutile was acquired from Sigma Aldrich. This rutile had no surface coating and was used to assess if the recovery process has an effect on the rutile itself or the surface coating of the pigment.

Table 1 Composition of paint used in pyrolysis experiments. . The weight percent of pigments within themselves is also given.

Component	Wt%	Wt% only pigments
	Total formulation	
Water	32.0%	
Surfactants	0.7%	
Coalescent aid	0.6%	
Biocide	0.2%	
Organic polymeric hiding additive	5.0%	
pH modifier	0.1%	
Cellulosic rheology modifier	0.7%	
Rheology modifier	0.2%	
Acrylic copolymer dispersion	33.6%	
Dolomite	11.1%	41.3%
Kaolin	1.2%	4.5%
Talc	1.2%	4.6%
Mica	1.2%	4.3%
Rutile	12.1%	45.2%

### 2.2 Methods for characterisation of pigments and inorganic recovery residues

#### 2.2.1 X-ray powder diffraction (XRD)

The main crystalline compounds in pigment samples were identified by qualitative X-ray powder diffractometry (XRD) using a Siemens D5000 X-ray powder diffractometer with the characteristic Cu radiation and a scintillation detector. The 2  $\Theta$  range used was 10-70 ° with a step size of 0.050 ° and a 1 second step time. The identification of compounds was performed through comparison with standards in the Joint Committee of Powder Diffraction Standards [Joint Committee of Powder Diffraction Standards, JCPDS-ICCD: PDF-4 release 2013 Philadelphia, USA]. Identification of a compound in a mixture is generally

possible if the compound is present in a concentration of 2% by weight or more. Amorphous compounds and compounds occurring in nano-sized crystals cannot be detected by XRD.

### *2.2.2 Thermo-gravimetric analysis (TGA)*

Thermo-gravimetric analysis (TGA) measurements on pigment mixtures were made in order to see how a thermal recycling process would affect the titanium dioxide and the extenders in the model paint. A non-pigment quality of rutile was also measured as reference to the titanium dioxide pigment. A nitrogen atmosphere was used to simulate the oxygen free atmosphere in a pyrolysis. All the pigments were measured on a NETZSCH STA 409 PC Luxx instrument and the non-pigment rutile was measured on a TA Instruments Q500 in the temperature interval 25-1000°C with a heating rate of 10°C per minute. Before starting of an experiment the furnace was evacuated twice and then filled with N<sub>2</sub>.

The heat stability of two binder samples, a vinyl acrylic latex copolymer with acrylic latex and a pure acrylic latex (see material section for more info), was investigated using the TGA Q500 from TA Instruments in the temperature range 25-600°C with a heating rate of 5°C per minute in inert atmosphere (N<sub>2</sub>) to simulate pyrolysis conditions.

### *2.2.3 Specific surface area by BET measurements*

The BET specific surface areas of the pigments, the pigment mix used in the model paint and the pyrolysis ashes before and after oxidative heat treatment were determined by N<sub>2</sub> adsorption isothermal at 77 K using a Micromeritics ASAP2020. Before measurement the samples were outgassed at 60°C under high vacuum (roughly 1 µm Hg) until the samples were considered dry or for maximum 1500 minutes. The samples were considered dry when the measured pressured change due to the sample was lower than 5 µmHg/min. The outgassing temperature has a significant effect on the BET result [15] so a relatively low outgassing temperature was chosen which was assumed not to alter the surface of the pigment.

## *2. 3 Microwave pyrolysis experiments*

The pyrolysis experiments were carried out in a pilot scale microwave pyrolysis furnace provided by Stena Metall AB, Göteborg. The dimensions of the pyrolysis chamber is 390x430x950 (mm) and with a total capacity of 10 L [16]. The microwaves are produced by three magnetrons of model Samsung OM 75P with a fixed frequency at 2465 MHz [16] and an individual power output for each magnetron of 1,5 kW. The sample container made of mica (transparent to microwaves) was used. The oven was flushed with nitrogen before each experiment. The liquid residue fraction was continuously collected during the experiment but the gas fraction was not collected. All temperatures were measured continuously at three points, inside the sample, at the surface the reaction vessel and the gas flow out from the furnace, see Figure 1. After the experiment the dry residue and the liquid oil fraction were weighed and saved for analysis. The amount of gas produced was estimated by subtraction of the dry and liquid residue fractions from the total weight prior to the experiments. In the present work the focus was on the inorganic parts of the sample materials and therefore the oil and gas fractions were not analysed further.

Four pyrolysis experiments were made, three on the paint formulation found in Table 1 and one on the same formulation but dried to a dry content of 65% prior to the pyrolysis experiment. Experiments 1 (wet paint) and 4 (dry paint) were designed for the initial evaluation of microwave pyrolysis as a method to recover the inorganic components from a waste paint. Experiments 2 and 3 were made on larger amounts of material in order to produce enough recycled pigment material to make it possible to manufacture a test paint based on a significant fraction of recycled pigments.



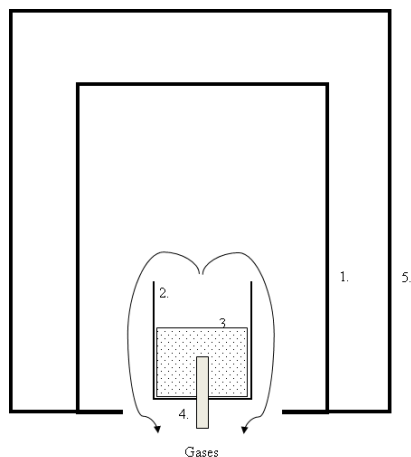


Figure 1 Schematic skis over the pyrolysis reactor used in the pyrolysis experiments

1. Reaction vessel; 2. Sample crucible; 3. Sample ;4. Thermocouple inside sample  
5. Outer casing. Continuously supplied with nitrogen gas.

#### 2.3.1 After-treatment and characterisation of ash from pyrolysis experiments 1, 2 and 3

The solid residue from pyrolysis experiment 1 was homogenized, weighed and put in a furnace and heated from 22°C to 400°C (the heating took 40min) in normal atmosphere and the temperature was then held at 400°C for 230 min. After cooling the sample was weighed and analysed with XRD. In addition, the effect of the after-treatment on the colour of the pyrolysed material was visually evaluated. This was done by placing samples of virgin rutile pigment, virgin dolomite, virgin mica, mix of virgin pigments corresponding to the one in the pyrolysis ash, grinded pyrolysis ash and heat treated pyrolysis ash next to each other on a white background and visually comparing the whiteness of each sample.

The solid residues from pyrolysis experiment 2 and 3 were mixed together and homogenized. This material was then divided into 10 sub-samples which were heat treated at 450°C in air during 3 hours. The weights before and after the heat treatments were recorded. After the heat treatment all the sub-samples were mixed together again to one sample and this material was analysed with XRD and BET.

#### 2.4 Evaluation of the properties of a paint based on recycled pigment material

To evaluate the potential of the pyrolysis ash as a pigment the combined after treated material from pyrolysis experiments 2 and 3 was incorporated into two formulations with high pigment volume concentration (PVC), see Table 2. To facilitate the formulation work the pyrolysis residue was simplified as a mixture of 45.2 weight percent  $\text{TiO}_2$  and 54.8 weight percent dolomite as these were the major components in the residues. The  $\text{TiO}_2$  in each formulation was substituted with the corresponding amount of ash on volume basis ( $\rho_{\text{TiO}_2} = 4.05 \text{ g/cm}^3$ ;  $\rho_{\text{dolomite}} = 2.85 \text{ g/cm}^3$ ) so the volume of  $\text{TiO}_2$  remained constant in standard paint and the paint based on recycled material. When needed virgin dolomite was added so the total volume of extenders remained the same as the assessed formulations. The properties of the paints made on recycled material were compared to properties of standard paints with same formulations but with virgin pigments and extenders. The experiment was classed as a success if the performance of the variants with recycled material matched all of the key paint properties of opacity, gloss, whiteness and durability of the standard paints. These properties were evaluated using test methods that are adapted from ISO tests, see Table 3.

Table 2 Paint Formulations used (expressed in wet volume in 100ml of paint). PVC stands for pigment volume concentration.

Material	High PVC formulation 1 With virgin material	High PVC formulation 1 With pyrolysis ash	High PVC formulation 2 With virgin material	High PVC formulation 2 With pyrolysis ash
Latex binder (50% solids)	5.3	5.3	4.4	4.4
Virgin TiO <sub>2</sub>	1.5	0.0	0.8	0.0
TiO <sub>2</sub> /Dolomite (recycled)	0.0	4.3	0.0	2.4
Virgin Dolomite	7.4	4.6	2.1	0.5
Other virgin extenders	18.6	18.6	19.4	19.4
Additives	0.6	0.6	1.0	1.0
Water	66.6	66.6	72.3	72.3

Table 3 Methods used to evaluate to paint produced on recycled material.

Test Method	Standard	Reference Number
Opacity(98% Spreading Rate)	ISO 6504-3	[17]
Whiteness	ASTM E313	[18]
Yellowness	ASTM E313	[18]
Gloss (85°)	ISO 2813	[19]
Durability (scrub resistance)	ISO 11998	[20]
Colour-difference (DE2k)	ISO 11664-6	[21]

### 3. Results and discussion

Note: To separate sample names from mineral names pigment samples will be written with capital letter and in italics.

#### 3.1 Characterisation of pigments with XRD and thermal stability

Three samples: TiO<sub>2</sub>, Kaolin and Dolomite, were identified with XRD as pure rutile, kaolinite-1A and dolomite respectively. Samples, Talc and Mica were both shown to contain more than one mineral. The XRD spectrum for Talc identified both talc and clinocllore and potentially a small amount of quartz. The Mica sample components were harder to identify however the major part seemed to be muscovite along with some kaolinite. Impurities are not uncommon as natural minerals are used as extenders. XRD results are summarized in Table 4 for each sample.

Table 4 Results from sample evaluation with XRD. Samples marked with (\*) are likely to contain some minor impurities.

Name of pigment sample	Compound identified by XRD	Chemical Formula
Dolomite	Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>
Kaolin	Kaolinite-1A	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
Talc*	Talc	Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>
	Clinocllore	(Mg,Al) <sub>6</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>
	Quartz	SiO <sub>2</sub>
Mica*	Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>
	Muscovite	KAl <sub>2</sub> (Si <sub>3</sub> Al)O <sub>10</sub> (OH,F) <sub>2</sub> or KAl <sub>2</sub> (SiAl) <sub>2</sub> O <sub>10</sub> (OH) <sub>2</sub>
TiO <sub>2</sub>	Rutile	TiO <sub>2</sub>

Results from the TGA, thermal analysis of the Dolomite sample showed this extender sample is stable at temperatures below 700°C. At higher temperatures (782 and 878 °C) two endothermic reactions occurred leading to the formation of magnesium oxide and calcium oxide [22, 23]. XRD spectrum for the residues from TGA experiments confirmed dolomite had decomposed into MgO (Periclase) and CaO (Lime). Theoretically a sample consisting of pure dolomite should in the first reaction give a mass loss (due to CO<sub>2</sub> emission) of 23.9% and the second calcination reaction should bring the total mass loss to 47.7%. TGA experiment showed an acceptable agreement with these theoretical mass losses.

TGA data gave a total mass loss of roughly 1.5% when the Rutile pigment was heated up to 1000°C. According to literature rutile is stable up to temperatures near 1800°C [24]. XRD analysis of the Rutile sample before and after TGA experiments verified that the crystal structure was intact. Burfield [25] got very similar results when heating pigment quality titanium dioxide with weight losses of 2-3%. Burfield explained this weight loss by decomposition of organic surface coatings on the pigment. Pigments are commonly treated with compounds to improve their dispersion in the paint systems [26]. The non-pigment quality rutile did not contain any surface modifications and showed no weight loss when heated up to 1000°C.

The Kaolin sample started endothermically decompose at 542°C. A comparison with literature data [27-29] suggests this is most likely due to dehydration of kaolin and the formation of meta-kaolin. The total mass loss was roughly 13%. This fits rather well with the loss of 2 water molecules per kaolin molecule during the dehydration which would give a mass loss of 14%. At 970°C a strong exothermic reaction was observed. This was most likely the transformation of meta-kaolin into a cubic spinel phase and amorphous silica [27-29]. Before the dehydration reaction of kaolin at 542°C a small mass loss of around 0.7% in the temperature range of 100-500°C was observed. This could be due to vaporisation of surface water, degradation of a surface coating or most likely is an effect of the instrument.

The TGA results for the Mica sample were comparable to those found in literature [30, 31]. Muscovite dehydroxylated over the temperature range of 475-950°C to final weight loss of 4-5%. The Mica still has a well ordered crystal structure after the TGA experiments, but there is not a complete agreement of the spectrum before and after TGA analysis so small changes in the crystal structure have probably occurred. This was not investigated further as these changes were assumed to occur in temperatures above 500°C.

The Talc sample decomposed via an endothermic reaction at 607°C and 835°C followed by an exothermic reaction at 870°C. According to a review article [32] the first major reaction during heating of talc is an endothermic reaction that dehydrates the material followed by various reactions where different crystalline and amorphous magnesium and silica oxides are formed depending on temperature. XRD analysis of the TGA residues showed only amorphous components were left most likely amorphous magnesium oxide and silica [32]. The transformation of talc into magnesium oxide and silica would give a theoretical mass loss of 4.8% in form of water vapour. The total mass loss in the present experiment was closer to 9%. This result, as well as the XRD results described earlier, suggested impurities in the talc sample.

Thermal and structural analysis of the pigment samples conclude that weight loss at low temperatures are probably due to loss of surface water and possible decomposition of organic coatings of the pigments. A pyrolysis process in temperatures below 500°C would leave the crystal structure of the majority inorganic pigments/extender unaffected.

### 3.2 Thermal stability of binders

The vinyl acrylic latex binder decomposed in two distinct steps at temperatures below 350°C in nitrogen atmosphere, see Figure 2. The decomposition continued continuously (no distinct steps due to low experimental resolution) at a temperature range of 350°C to 500°C until a residue weight 5% of the original sample weight remained. The binder based on pure acrylic polymer decomposed in a single step in the temperature range of 310 to 400°C to a residue weighing 3% of the original sample weight in nitrogen atmosphere, see Figure 3.

The thermal decomposition of these binder samples could be studied in greater detail but the aim of this study was mainly to see in which temperature range the binders start to decompose into volatile products. The result shows that a thermal process, such as pyrolysis, at 500°C would be sufficient to make most of the binders in waste paint mixture decompose.

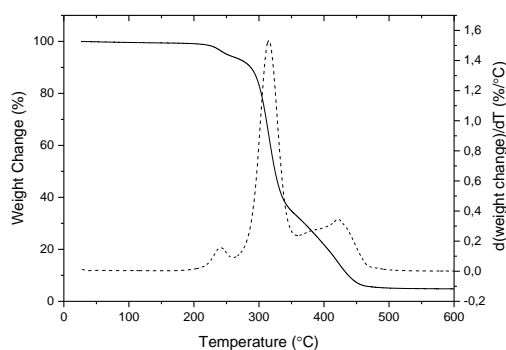


Figure 2 TGA results of vinyl acrylic latex in nitrogen atmosphere.

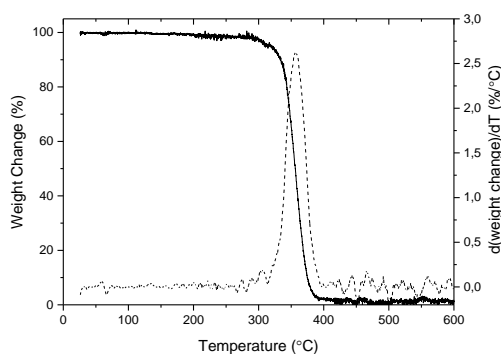


Figure 3 TGA results of pure acrylic polymer in nitrogen atmosphere.

### 3.3 Pyrolysis of the model paint

Pyrolysis experiments were carried out on wet paint (experiments 1-3) and dried paint (experiment 4) samples. The paint used in experiment 4 had been dried to a dry content of 65% (compared to 44% for the other experiments) prior to the pyrolysis. When the weight fraction of the inorganic components (dolomite, kaolin clay, talc, mica and rutile) for the wet paint it is concluded that inorganics make up 26.8wt% of the total sample, see Table 1. While the dry paint is composed of 57wt% inorganic compounds. Theoretically the dry pyrolysis residue should contain all the inorganic components in the paint due to the volatile nature of the organics at higher temperature. The measured and calculated value show good agreement for experiments 1 and 2. In experiment 3 the residue is somewhat larger but still in the same size range meaning there was a small amount of organic matter that was not completely pyrolysed in experiment 3. This could be confirmed as pieces of non-pyrolysed paint could be found in the residues. In experiment 4 the lack of water in the sample made it difficult to get uniform heating of the material resulting in incomplete pyrolysis where large particles of non-decomposed paint were still present after the pyrolysis even though the experiment was continued for 100 minutes. Complete volatilization of the organic components would have resulted in a dry residue of 57wt% (higher than the other experiments due drying before pyrolysis). The solid residue from experiment 4 was 64 wt% (see Table 5) this is also an indication of incomplete pyrolysis. This shows that microwave pyrolysis is not suitable for treatment of dry paint.

Table 5 Weight of samples before and after pyrolysis. The weight percent is the ratio of the residue fraction over the sample mass prior to heating.

Sample	Experiment 1		Experiment 2		Experiment 3		Experiment 4	
	wt (g)	wt%	wt (g)	wt%	wt (g)	wt%	wt (g)	wt%
Sample, prior to heating	241	100%	1450	100%	1624	100%	245	100%
Liquid fraction	112	47%	850	59%	1021	63%	52	21%
Dry fraction	66	27%	398	27%	468	29%	157	64%
Gas fraction (calculated)	63	26%	202	14%	135	8%	37	15%

### 3.4 After-treatment of pyrolysed paint from pyrolysis experiment 1

After the heat treatment in air the solid residues from pyrolysis experiment 1 gave a weight loss of 4%. Heat treatment of the solid residue in the presence of oxygen significantly increased the whiteness of the sample as shown in Figure 4. The weight change and the change in colour are probably due to the oxidation of char carbon to carbon oxides. However, even if the whiteness is improved by the heat treatment the colour is still far from the colour of a mix containing virgin pigments.



Figure 4 From left to right. Virgin rutile pigment, virgin dolomite extender, virgin Mica extender, mix of virgin pigments corresponding to the one in the pyrolysis ash, grinded pyrolysis ash, heat treated pyrolysis ash.

XRD spectrums of the ground pyrolysis residue, before and after heat treatment are shown in Figure 5 and Figure 6. The solid residue from the pyrolysis process only consists of the inorganic pigments of the pyrolysed paint, see Table 1, rutile and dolomite together make up almost 90wt% of the total residue. This explains their dominance in the XRD spectrum. The difference in peak height for some of the rutile peaks (Figure 6) is most likely due to a preferred orientation of crystals and not to a change in mineral concentration during the after treatment.

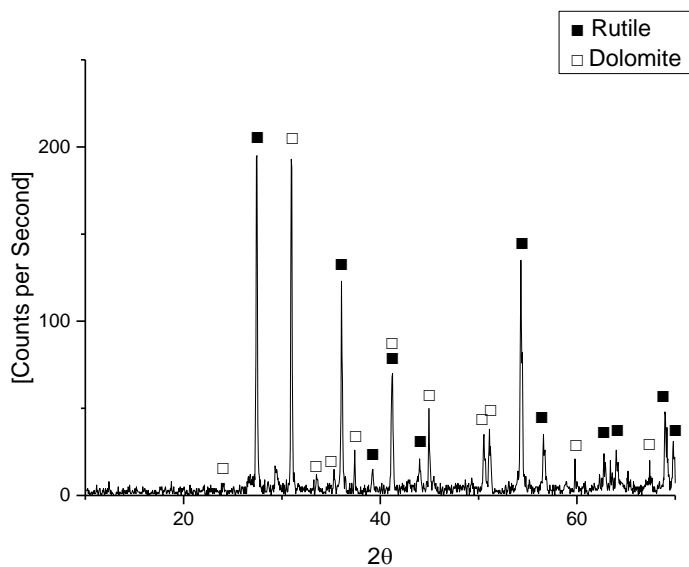


Figure 5 XRD spectrum of grinded dry residues from pyrolysis experiment 1. Peaks for Rutile (■) and Dolomite (□) are marked out.

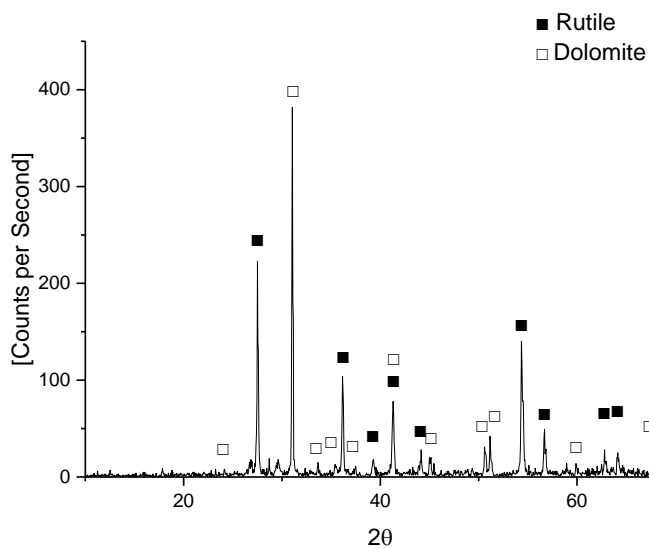


Figure 6 XRD spectrum of dry residues from pyrolysis experiment 1 heated to 400°C in normal atmosphere for 230 minutes. Peaks for Rutile (■) and Dolomite (□) are marked out.

Based on the XRD results the crystal structure of rutile and dolomite seem to be unaffected by both the pyrolysis process and the after-treatment in normal atmosphere. This is consistent with the previously presented results from the TGA experiments showing rutile and dolomite the most temperature durable pigments of those studied. Since it was shown that the pigments themselves are unaffected by the heat treatment in air it should be possible to get a whiter pigment by oxidizing the remaining residues of carbon containing compounds in the presence of oxygen or another oxidizing agent.

### *3.4 After-treatment of pyrolysed paint from pyrolysis experiment 2 and 3*

The recorded weights of samples of mixed material from pyrolysis experiments 2 and 3 before and after heat treatment in air are shown in Table 6. In these experiments the weight loss due to the oxidative heat treatment was roughly 6-7%. The variations in weight loss between samples are likely caused by inhomogeneity in the pyrolysed material and slight variations in temperature during oxidation.

Table 6 Weights of mixed solid residues from pyrolysis experiment 2 and 3 before and after 450°C for 180 minutes in air

<b>Weight before heat treatment [g]</b>	<b>Weight after heat treatment [g]</b>	<b>Remaining material after oxidation</b>
<b>50.31</b>	47.12	93.7%
<b>49.05</b>	45.59	92.9%
<b>52.15</b>	48.74	93.5%
<b>50.40</b>	47.07	93.4%
<b>54.28</b>	50.73	93.5%
<b>64.64</b>	60.51	93.6%
<b>61.71</b>	57.90	93.8%
<b>67.85</b>	63.79	94.0%
<b>62.33</b>	58.49	93.8%
<b>50.36</b>	47.48	94.3%

XRD spectrum for the mixed material from pyrolysis experiments 2 and 3 after the heat treatment in air showed the crystal structure of the components. Dolomite and rutile are intact similar to what was observed for the oxidised residues from pyrolysis experiment 1, see Figure 7. The spectra seen in Figure 7 are for the heat treated residues from pyrolysis experiment 1 (topmost), pyrolysis experiment 2 (middle) and pyrolysis experiment 3 (bottom).

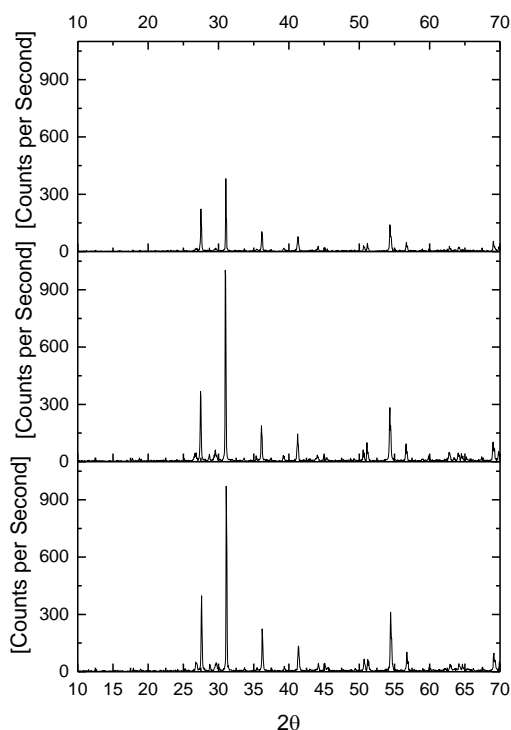


Figure 7 XRD of heat treated residues from pyrolysis experiment 1 (topmost), pyrolysis experiment 2 (middle) and pyrolysis experiment 3 (bottom).

### 3.5 Effect of pyrolysis and oxidative after-treatment on specific surface area

Results from BET measurements on different sample materials are shown in

Table 7 for residues in experiment 2 and 3 and Table 8 for the virgin material. There is no significant difference before and after the heat treatment of the pyrolysis residues. A sintering effect may have given reduced surface area. This combined with the XRD results presented previous suggest the heat treatment in air does not affect the pigments in a negative way. However, the specific surface area of the pyrolysis residues is significantly smaller than that of the starting pigment mix. This suggests an agglomeration of the pigments and extenders during the pyrolysis process occurs even though the XRD shows that the crystal structure structures are intact. The data for the virgin pigments studied one by one are shown in Table 8. Here the surface area for all pigment except rutile is intact after a heat treatment at 450°C. The non-pigment rutile is also unaffected. This shows that the rutile pigment is affected by the heat treatment and probably an agglomeration of particles has occurred. This may be due to decomposition of the surface coating of the pigment. If this is true it will have an effect on the properties on paint film in which the pigment is incorporated.



Table 7 Result from BET measurements made in triplicates on pigments and mixed pyrolysis residues from experiment 2 and 3 before and after heat treatment in air 450°C for 180 minutes and a mix of virgin pigments corresponding to the pigments in the pyrolysed paint.

Sample	BET [m <sup>2</sup> /g]	
	Average	Std.Dev
<b>Pyrolysis Residue</b>	6.33	0.11
<b>Heat treated Residue</b>	6.53	0.27
<b>Pigment mix</b>	9.71	0.31

Table 8 Result from BET measurements on virgin pigments before and after a heat treatment in air 450°C for 180 minutes.

Pigment sample	Mass loss due to heat treatment	BET [m <sup>2</sup> /g]	
		Before	After
<b>Dolomite</b>	0.3%	0.80	0.68
<b>Kaolin</b>	9.7%	14.49	14.47
<b>Talc</b>	0.2%	4.86	4.25
<b>Mica</b>	1.6%	3.51	3.02
<b>Rutile</b>	1.3%	17.24	12.21
<b>Non-pigment rutile</b>	0.0%	2.64	2.66

### 3.6 Paint properties of paint based on recycled material

All methods used for evaluation of the paints based on virgin and recycled material along with the results are given in Table 9. Before the impact on performance based on the inclusion of the pyrolysis residues can be discussed, some experimental observations need to be considered. Firstly, the recycled material was not fully dispersed into the paint system resulting in film defects (lumps) seen in lower half of Figure 8. This effect was seen even when increased dispersant levels were added to the formulation. Secondly, the change in colour from the raw material causes false positives in some of the paint testing. The grey colour impacts the opacity results as the calculation is based on coverage over a white and black area which can be impacted by paint colour.

Table 9 Results of paint parameters for paint based on virgin and recycled material

	Method	High PVC formulation 1	High PVC formulation 1	High PVC formulation 2	High PVC formulation 2
		With virgin material	With pyrolysis ash	With virgin material	With pyrolysis ash
Opacity(98% Spreading Rate)	ISO 6504-3	8.3	11.0	5.6	7.6
Whiteness	ASTM E313	83.15	78.11	80.90	74.75
Yellowness	ASTM E313	2.88	3.34	3.50	3.80
Gloss (85°)	ISO 2813	14.9	12.3	10.4	9.6
Durability (scrub resistance)	ISO 11998	0.9	1.3	8.9	11.1
Colour-difference	ISO 11664-6	N/A	1.1	N/A	1.6

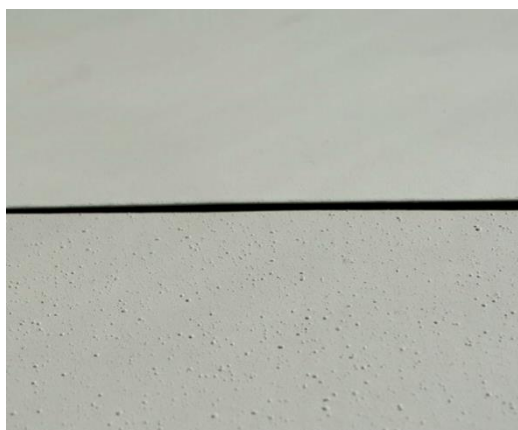


Figure 8 Picture of paint films made with virgin pigments (top) and recycled pigments (bottom). Real length of paint sample shown is 10cm.

To help describe the paint results expected measuring values for different paint qualities are shown in Table 10. Substitution of the recycled materials for the virgin pigments has impacted the product performance by changing it from a Mid Tier Matt performance to a Low Tier Matt performance in terms of whiteness and yellowness. The point of interest that was highlighted with these results was that the effect on whiteness is more significant than the effect seen on the yellowness. Although whiteness and yellowness are generally secondary paint properties, an indicative change in acceptable results for these in absolute terms would be whiteness decrease of 1 to 1.5 units and yellowness increase of 0.3-0.5 units.

Table 10 Simplified overview of expected whiteness and yellowness of different formulation types. Standard data given by Akzo Nobel Decorative Paints.

Formulation Type	TiO <sub>2</sub> content	Expected Whiteness Range	Expected Yellowness Range
<b>Silk/Softsheen/Premium Matt</b>	High	91 – 86	1.0 – 2.0
<b>Mid Tier Matt</b>	Moderate	86 – 82	2.0 – 3.0
<b>Low Tier Matt</b>	Low	82 – 78	3.0 – 4.0

Based only on the whiteness and yellowness range the true extent of performance impact of the recycled material is difficult to make a conclusion. The results of the key properties can be expressed as:

- Opacity – a false positive was observed based on the grey hue of the paint influencing the spreading rate calculations (this method includes absorption and scatter contributions so the colour will have an impact of the observations).
- Gloss - equivalent for both formulations (film defect problem is hidden by matt formulations).
- Whiteness and yellowness index – significant drop in paint whiteness (large impact by grey nature of the recycled TiO<sub>2</sub>) but equivalent yellowness.
- Durability – slightly reduced performance (based on increased dispersant levels).

From these experimental results it can be concluded that recycled pigments cannot be used as a direct replacement in paint formulations. However, before the material can be approved or rejected for use in formulating the issues with bad dispersion and colour change needs to be resolved. To ensure the pyrolysis residues has been properly used dispersant demand needs to be investigated to ensure the correct level and type of dispersant is used in when formulating with this material. The level and type of dispersant are

dependent on the surface chemistry of the recycled pigment.

#### **4. Conclusion**

In this work a model paint containing several different types on inorganic pigments was pyrolysed in a micro wave heated unit. The TGA analysis of these pigment samples showed that a pyrolysis process in temperatures below 500°C should leave the crystal structure of the inorganic pigments/fillers unaffected. The TGA results of binder samples revealed that a thermal process, such as pyrolysis, at 500°C would be sufficient to make most of the binders in waste paint mixture decompose. It was also concluded that the solid residue from the pyrolysis process could be further heat treated in the presence of oxygen to improve the whiteness of the residue without affecting the crystal structure of the inorganic components.

When the heat treated pyrolysis residues was used in paint formulations as titanium dioxide replacement was a significant drop in paint whiteness observed but the opacity, gloss and durability was almost equivalent to the standard paint. Another serious issue was an inferior dispersibility of the recycled mix of pigments and extenders in the paint. This gave the painted surface a rough texture which is not wanted. The conclusion reached was that the recycled material showed promises as a pigment but further studies are needed to make it possible to incorporate it in paint formulations in the best way. To understand the poor dispersibility of the pigment the surface chemistry of the pigment needs to be investigated further.

Further investigations into how the recycling process affects the surface of the pigment will be carried out with SEM dispersant demand tests and titration of acid/base surface groups. When these factors have been investigated, new pyrolysis and oxidation experiments will be designed to optimise the recovery of pigments. Due to the difficulties to control the temperature distribution in the micro wave heated pyrolysis unit and the difficulties to treat dry paint that heating method will be replaced by an electrically heated oven. The possibility of a surface treatment to be added to the recovered pigments to improve their dispersibility will also be investigated.

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